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Researches
in
Organic Chemistry

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Researches in Organic Chemistry

Carried out in the

University of Aberdeen

By

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Reduction Products of αβ-Dimethylanhydracetonebenzil, and Condensation Products of Benzaldehyde with Ketones.

By FRANCIS ROBERT JAPP, F.R.S., and WILLIAM MAITLAND, B.Sc., Carnegie Fellow in the University of Aberdeen.

WE find that when αβ-dimethylanhydracetonebenzil (compare Japp and Burton, Trans., 1887, 51, 432; Japp and Meldrum, 1901, 79, 1036) is boiled for five minutes with fuming hydriodic acid, it is reduced to 4:5-*diphenyl*-1:3-*dimethyl*cyclo*penten*(4)-*one*(2), melting at 122°:

$$\left.\begin{array}{l} C_6H_5\cdot C{=\!=\!=\!=}C(CH_3) \\ C_6H_5\cdot C(OH)\cdot CH(CH_3)\end{array}\right\rangle CO + 2H = \left.\begin{array}{l} C_6H_5\cdot C\cdot CH(CH_3) \\ C_6H_5\cdot C\cdot CH(CH_3)\end{array}\right\rangle CO + H_2O.$$

This change in the position of the double bonds is of general occurrence in the reduction of anhydracetonebenzil derivatives to *cyclo*pentenones (compare Japp and Murray, Trans., 1897, 71, 145; Japp and Meldrum, 1901, 79, 1026).

The foregoing product is identical with the substance of the same melting point obtained, along with other compounds, by the reduction of 4:5-diphenyl-1:3-dimethyl-1:4:5-trihydroxy*cyclo*pentanone(2),

$$\left.\begin{array}{l} C_6H_5\cdot C(OH)\cdot C(OH)(CH_3) \\ C_6H_5\cdot C(OH){-\!-\!-}CH(CH_3)\end{array}\right\rangle CO,$$

with hydriodic acid (Japp and Michie, Trans., 1903, 83, 303). It is, moreover, identical with the compound to which Vorländer and Wilcke (*Ber.*, 1898, 31, 1887) ascribe the constitution of a dibenzylidenediethyl ketone, $\left.\begin{array}{l} C_6H_5\cdot CH{:}C(CH_3) \\ C_6H_5\cdot CH{:}C(CH_3)\end{array}\right\rangle CO$, a view of its constitution which, as we shall now show, must be abandoned, as the reactions of the compound prove that it contains the *cyclo*pentenone group.

Petrenko-Kritschenko and Plotnikoff (*Ber.*, 1897, 30, 2801) had obtained dibenzylideneacetone by warming an alcoholic solution of diphenyltetrahydro-γ-pyrone to which a few drops of hydrochloric acid had been added:

$$\left.\begin{array}{l} C_6H_5-CH\cdot CH_2 \\ \quad O\langle \\ C_6H_5-CH\cdot CH_2\end{array}\right\rangle CO = \left.\begin{array}{l} C_6H_5\cdot CH{:}CH \\ \\ C_6H_5\cdot CH{:}CH\end{array}\right\rangle CO + H_2O.$$

Vorländer and Wilcke (*loc. cit.*) tried whether the same treatment would convert Vorländer and Hobohm's diphenyldimethyltetrahydro-γ-pyrone (*Ber.*, 1896, 29, 1352) into dibenzylidenediethylketone, but found that under these conditions no change occurred. However, by passing gaseous hydrogen chloride for two hours into a boiling solution of diphenyldimethyltetrahydro-γ-pyrone in glacial acetic acid and allowing the mixture to remain for some days, they succeeded in transforming this substance into a compound having the expected composition, which they regarded as dibenzylidenediethyl ketone. Under this more drastic treatment, however, the γ-pyrone derivative is dehydrated, not on the lines of Petrenko-Kritschenko and Plotnikoff's reaction, as Vorländer and Wilcke assume, but according to the scheme :

$$\begin{array}{l} C_6H_5-CH\cdot CH(CH_3) \\ \;\;O\langle \\ C_6H_5-CH\cdot CH(CH_3) \end{array} \!\!>\!CO \;=\; \begin{array}{l} C_6H_5\cdot C\cdot CH(CH_3) \\ \qquad\;\, \| \\ C_6H_5\cdot C\cdot CH(CH_3) \end{array} \!\!>\!CO + H_2O,$$

Diphenyldimethyl-tetrahydro-γ-pyrone. 4 : 5-Diphenyl-1 : 3-dimethyl-*cyclo*penten(4)-one(2).

the carbon chain closing in the process.

Vorländer and Wilcke (*loc. cit.*) believed that they had obtained confirmation of their view as to the constitution of the foregoing compound in the fact that it yields with bromine a substance which they regarded as dibenzylidenediethyl ketone tetrabromide. This bromine derivative, however, is only partly additive; it is *diphenyldimethyldibromo*cyclo*pentenone dibromide*, or better, *diphenyldimethyltetrabromo*cyclo*pentanone*, $\begin{array}{l} C_6H_5\cdot CBr\cdot CBr(CH_3) \\ C_6H_5\cdot CBr\cdot CBr(CH_3) \end{array}\!\!>\!CO$. Hydrogen bromide is evolved during its formation, and it contains in its molecule 2 atoms of hydrogen fewer than would be required by the formula ascribed to it by Vorländer and Wilcke.

We have ascertained that diphenyl*cyclo*pentenone interacts in a similar manner with bromine, yielding *diphenyltetrabromo*cyclo*pentanone*:

$$\begin{array}{l} C_6H_5\cdot C\cdot CH_2 \\ C_6H_5\cdot C\cdot CH_2 \end{array}\!\!>\!CO + 3Br_2 \;=\; \begin{array}{l} C_6H_5\cdot CBr\cdot CHBr \\ C_6H_5\cdot CBr\cdot CHBr \end{array}\!\!>\!CO + 2HBr.$$

Vorländer and Mumme (*Ber.*, 1903, 36, 1477) found that the supposed dibenzylidenediethyl ketone, unlike dibenzylideneacetone and other doubly unsaturated ketones of this type, did not form an additive compound with hydrogen chloride. The explanation lies in the fact that it differs entirely in constitution from these.

Again, Mentzel (*Ber.*, 1903, 36, 1499) draws certain theoretical conclusions from the facts (1) that the supposed dibenzylidenediethyl ketone is "almost colourless" (it is quite colourless when pure) and (2) that it gives hardly any coloration with concentrated sulphuric

acid. He seeks to explain its apparently exceptional behaviour in these respects, compared with that of various authentic dibenzylidene derivatives of ketones. No explanation is necessary; its behaviour is that of the other *cyclo*pentenones obtained by the reduction of anhydracetonebenzil and its derivatives.

Although the description which Petrenko-Kritschenko and Plotnikoff (*loc. cit.*) give of the compound $C_{17}H_{14}O$, which they prepared by the action of alcoholic hydrochloric acid on diphenyltetrahydro-γ-pyrone, left little doubt that this substance was, as they assert, dibenzylideneacetone, and not the isomeric diphenyl*cyclo*pentenone, we nevertheless repeated their experiment, as the nearness of the melting points of the two isomerides—dibenzylideneacetone 112°, diphenyl*cyclo*pentenone 110°—rendered just possible a confusion between the two substances. We found, however, that the product was undoubtedly dibenzylideneacetone, a result which we confirmed by the mixture melting-point test.

By boiling diphenyldimethyl*cyclo*pentenone (m. p. 122°), prepared by Vorländer and Wilcke's method, with hydriodic acid and red phosphorus for $1\frac{1}{2}$ hours, it is reduced to 4 : 5-*diphenyl*-1 : 3-*dimethyl*cyclo-*pentanone*(2), $\begin{matrix} C_6H_5\cdot CH\cdot CH(CH_3) \\ | \\ C_6H_5\cdot CH\cdot CH(CH_3) \end{matrix}\!\!>\!CO$, which, like the *cyclo*pentenone from which it is formed, melts at 122°. In appearance, it is almost indistinguishable from the latter compound. It forms an *oxime* (m. p. 165·5°) and a *dibromo*-derivative, $\begin{matrix} C_6H_5\cdot CH\cdot CBr(CH_3) \\ | \\ C_6H_5\cdot CH\cdot CBr(CH_3) \end{matrix}\!\!>\!CO$ (m. p. 192° with decomposition).

This diphenyldimethyl*cyclo*pentanone is more conveniently obtained by boiling $\alpha\beta$-dimethylanhydracetonebenzil for some time with hydriodic acid and red phosphorus, the *cyclo*pentenone which is first formed being thus further reduced.

It may also be prepared in the same way from diphenyldimethyltetrahydro-γ-pyrone.

Diphenyldimethyl*cyclo*pentenone (m. p. 122°) and diphenyldimethyl*cyclo*pentanone, when dissolved together in equal quantities, form mixed crystals, perfectly homogeneous in appearance, melting at 102—103°, and having a specific gravity which is almost exactly the mean of those of the two pure substances. Mixed crystals of a different melting point can, however, also be obtained, showing that their composition is not constant. We first obtained these mixed crystals in an experiment in which diphenyldimethyltetrahydro-γ-pyrone was boiled for only a few minutes with hydriodic acid, and their formation under these circumstances shows that diphenyldimethyl*cyclo*pentenone is the first product in the transformation of the γ-pyrone derivative into diphenyldimethyl*cyclo*pentanone by hydriodic acid in the reaction just described.

Dibenzylideneacetone, when reduced with hydriodic acid, yielded only a gum from which nothing definite could be isolated. It behaves in a totally different manner from the supposed dibenzylidenediethyl ketone.

In condensing benzaldehyde with diethyl ketone to obtain the diphenyldimethyltetrahydro-γ-pyrone required for the present research, we employed a stronger solution of potassium hydroxide than is prescribed by Vorländer. We thus obtained, along with the expected γ-pyrone derivative, a compound formed from it by the removal of the elements of a molecule of water. This new compound, which melts at 128°, is readily prepared from diphenyldimethyltetrahydro-γ-pyrone by leaving it in contact with alcoholic potassium hydroxide in the cold. It is 4 : 5-*diphenyl*-1 : 3-*dimethyl*cyclo*penten*(5)-*one*(2), and is formed as follows:

$$O<\begin{array}{l} C_6H_5\text{—}CH\cdot CH(CH_3) \\ C_6H_5\text{—}CH\cdot CH(CH_3) \end{array}>CO = \begin{array}{l} C_6H_5\cdot C{=\!=}C(CH_3) \\ C_6H_5\cdot CH\cdot CH(CH_3) \end{array}>CO + H_2O.$$

We shall give later on our reasons for assigning this constitution to the compound; but it may be noted here that diphenyldimethyltetrahydro-γ-pyrone yields by dehydration two different diphenyldimethyl*cyclo*pentenones (that of m. p. 122° and that of m. p. 128°) according as hydrogen chloride or potassium hydroxide is employed as a dehydrant.

The diphenyldimethyl*cyclo*pentenone melting at 128° is transformed, by warming it with alcohol to which a few drops of hydrochloric acid have been added, into the isomeride melting at 122°; but an attempt to effect the reverse change by heating the latter compound with alcoholic potassium hydroxide gave only an amorphous product.

The present diphenyldimethyl*cyclo*pentenone (m. p. 128°) yields an *oxime* (m. p. 121·5°), a *dibromide*, $\begin{array}{l} C_6H_5\cdot CBr\cdot CBr(CH_3) \\ C_6H_5\cdot CH\text{—}CH(CH_3) \end{array}>CO$ (m. p. 185°, with decomposition), and, by reduction with hydriodic acid, is converted into diphenyldimethyl*cyclo*pentanone (m. p. 122°) identical with the substance of that constitution already described.

A compound, $C_{18}H_{18}O_2$, which, from its modes of formation, might be diphenylmethyltetrahydro-γ-pyrone, $O<\begin{array}{l} C_6H_5\text{—}CH\cdot CH(CH_3) \\ C_6H_5\text{—}CH\text{———}CH_2 \end{array}>CO$, has been prepared by Levinstein (*Inaugural-Diss.*, Berlin, 1902) by the condensation of 2 mols. of benzaldehyde with 1 of methyl ethyl ketone under the influence of sodium hydroxide, and by Harries and Müller (*Ber.*, 1902, 35, 968) by condensing in a similar manner benzaldehyde with α-benzylidenemethyl ethyl ketone.

Levinstein found, as the melting point of the condensation compound, 74°; Harries and Müller, 68·5°.

As it appeared possible that this compound might, like diphenyldimethyltetrahydro-γ-pyrone, be converted, by treatment with hydrochloric acid, or hydriodic acid, or potassium hydroxide, into compounds containing a pentacarbon ring, we prepared it by the two foregoing methods. In both cases we obtained a mixture of two isomeric compounds of the empirical formula $C_{18}H_{18}O_2$, melting respectively at 82—83° and 102—103°. These could be separated by crystallisation, and we believe that the discrepant and much too low melting points observed by Levinstein, on the one hand, and Harries and Müller, on the other, are due to the fact that these investigators were dealing with mixtures of the two compounds. Possibly they are stereoisomeric diphenylmethyltetrahydro-γ-pyrones; but as they could not be converted into either of the known compounds of which we were in search—diphenylmethyl*cyclo*pentenone and diphenylmethyl*cyclo*pentane—we did not investigate them further.

Experimental.

I. 4:5-*Diphenyl*-1:3-*dimethyl*cyclo*penten*(4)-*one*(2),

$$\begin{matrix} C_6H_5\cdot C\cdot CH(CH_3) \\ \| \\ C_6H_5\cdot C\cdot CH(CH_3) \end{matrix} \!\!>\! CO.$$

Eight grams of finely-powdered $a\beta$-dimethylanhydracetonebenzil, $\begin{matrix} C_6H_5\cdot C{=\!=\!=\!=}C(CH_3) \\ | \\ C_6H_5\cdot C(OH)\cdot CH(CH_3) \end{matrix}\!\!>\!CO$ (m. p. 150°), were boiled for 5 minutes over a free flame with an excess of fuming hydriodic acid (sp. gr. 1·96). The product was precipitated with water and dissolved in ether; the ethereal solution was successively treated with solutions of sulphurous acid and sodium carbonate; and the neutral substance which remained after expelling the ether was purified by distillation under 12 mm. pressure and subsequent recrystallisation from alcohol, from which it was deposited in colourless scales, melting constantly at 122°.

Analysis gave figures agreeing with the formula of the expected *diphenyldimethyl*cyclo*pentenone.*

0·1599 gave 0·5086 CO_2 and 0·0987 H_2O. C = 86·74; H = 6·85.
0·1552 „ 0·4919 CO_2 „ 0·0978 H_2O. C = 86·44; H = 7·00.
$C_{19}H_{18}O$ requires C = 87·02; H = 6·87 per cent.

Different specimens were used for analysis.

By spontaneous evaporation from a solution in ethyl acetate with the addition of light petroleum, the substance is obtained in clear, prismatic crystals, showing an extinction angle of about 34° from the vertical axis, having a sp. gr. of 1·1775 at 15°, and melting as above

at 122°. Sometimes the prisms are flattened, causing them to assume a tabular habit.

Japp and Michie (Trans., 1903, 83, 303) prepared this compound for the purpose of comparing it with the substance of the same melting point and same composition which they had obtained by the reduction of diphenyldimethyltrihydroxy*cyclo*pentanone with hydriodic acid, and found that the two were identical.

As this diphenyldimethyl*cyclo*pentenone agreed also in properties and composition with the substance which Vorländer and Wilcke (*Ber.*, 1898, 31, 1887) obtained by the action of hydrogen chloride on diphenyldimethyltetrahydro-γ-pyrone and which they regard as dibenzylidenediethyl ketone, we prepared this supposed dibenzylidenediethyl ketone according to their method. No difference in physical properties between the substances obtained by the two methods could be detected. Both melted at 122°, and no depression of melting point was observed on mixing the two specimens.

As no case is known of the formation of an open-chain compound by the reduction of anhydracetonebenzil derivatives with hydriodic acid—as these substances, on the contrary, all yield, as first stage of the reduction, *cyclo*pentenone derivatives containing the complex $C_6H_5\cdot\underset{|}{C}:\underset{|}{C}\cdot C_6H_5$—we ascribe to Vorländer and Wilcke's supposed dibenzylidenediethyl ketone the *cyclo*pentenone constitution already given.

The oxime (m. p. 157—159°) which they describe (*loc. cit.*) has therefore the constitution $\begin{matrix} C_6H_5\cdot C\cdot CH(CH_3) \\ \| \\ C_6H_5\cdot C\cdot CH(CH_3) \end{matrix}\!\!>C:N\cdot OH.$

*Action of Bromine on Diphenyldimethyl*cyclo*pentenone* (m. p. 122°).—Vorländer and Wilcke (*loc. cit.*) assert that their "dibenzylidenediethyl ketone" forms an additive compound with 4 atoms of bromine. This observation, if correct, would form a very strong argument in favour of the constitution which they ascribe to this substance. We, therefore, repeated their experiment, adhering strictly to the conditions which they prescribe.

One and a half grams of diphenyldimethyl*cyclo*pentenone (m. p. 122°), prepared by Vorländer and Wilcke's method, were dissolved in chloroform, 4 grams of bromine were added, and the whole was left for 24 hours. Although the materials had been carefully dried, hydrogen bromide was evolved in the reaction. After expelling the solvent and the excess of bromine at the ordinary temperature by means of a current of dry air, and recrystallising the residue from benzene with the addition of methyl alcohol, the substance was obtained in small, oblique, four-sided plates, melting at about 180° with previous decomposition. This agrees with Vorländer and Wilcke's description

0·2414 gave 0·3140 AgBr. Br = 55·35.

$C_{19}H_{16}OBr_4$ requires Br = 55·17 per cent.

Vorländer and Wilcke's analyses agree better with this formula than with that which they assign to the compound. The value for hydrogen is decisive. Thus, whilst $C_{19}H_{16}OBr_4$ requires H = 2·76, Vorländer and Wilcke's formula, $C_{19}H_{18}OBr_4$, requires H = 3·09 per cent. They find H = 2·8 per cent. This value, together with the fact that hydrogen bromide is evolved in the formation of the substance, decides in favour of the formula $C_{19}H_{16}OBr_4$. The compound is formed by the addition of 2 atoms of bromine to diphenyldimethyl*cyclo*pentenone and the substitution of 2 further atoms of bromine for hydrogen in the resulting compound. The substance is therefore *diphenyldimethyltetrabromo*cyclo*pentanone*, $\begin{array}{l} C_6H_5\cdot CBr\cdot CBr(CH_3) \\ \quad\;\; | \\ C_6H_6\cdot CBr\cdot CBr(CH_3) \end{array}\!\!>\!CO.$

*Action of Bromine on Diphenyl*cyclo*pentenone*, $\begin{array}{l} C_6H_5\cdot C\cdot CH_2 \\ \quad\;\; \| \\ C_6H_5\cdot C\cdot CH_2 \end{array}\!\!>\!CO.$—The following experiment shows that diphenyl*cyclo*pentenone, the first product of the reduction of anhydracetonebenzil with hydriodic acid, behaves towards bromine like its dimethyl homologue.

Half a gram of diphenyl*cyclo*pentenone (m. p. 110°) was dissolved in chloroform and treated with 1·3 grams of bromine. Hydrogen bromide was evolved, and the solution, when left overnight, deposited reddish crystals. The mixture was left for 2 days and then treated as in the previous case. The crystalline residue was dissolved in alcohol, from which it was deposited in slender, colourless needles, which sinter and turn red at 120°, melting completely at about 130° (yield 0·4 gram).

0·1944 gave 0·2658 AgBr. Br = 58·19.

$C_{17}H_{12}OBr_4$ requires Br = 57·97 per cent.

The compound is a *diphenyltetrabromo*cyclo*pentanone*, doubtless of the constitution $\begin{array}{l} C_6H_5\cdot CBr\cdot CHBr \\ \quad\;\; | \\ C_6H_5\cdot CBr\cdot CHBr \end{array}\!\!>\!CO.$

It is readily decomposable, and in two subsequent attempts which we made to prepare it, in order to obtain material for a complete analysis, there was formed instead, probably by splitting off of hydrogen bromide from the tetrabromo-derivative, a compound melting at about 190—200°. This was not further examined.

We also tried the action of bromine under similar conditions on diphenylmethyl*cyclo*pentenone (compare Japp and Meldrum, Trans., 1901, **79**, 1032), but as we failed to obtain the product in a crystallisable form, we did not examine it further.

II. 4 : 5-*Diphenyl*-1 : 3-*dimethyl*cyclo*pentanone*(2),

$$\begin{matrix} C_6H_5\cdot CH\cdot CH(CH_3) \\ | \\ C_6H_5\cdot CH\cdot CH(CH_3) \end{matrix} > CO.$$

Nine grams of $\alpha\beta$-dimethylanhydracetonebenzil, 18 grams of red phosphorus, and 135 grams of hydriodic acid (sp. gr. 1·7) were boiled together for 1½ hours. The resulting solid mass was separated from the excess of acid, pulverised, washed with water, and extracted with ether. The ethereal extract was successively shaken with solutions of sulphurous acid and sodium carbonate. On expelling the ether a crystalline mass remained, which was purified by recrystallisation, first from light petroleum (b. p. 50—80°) and afterwards from alcohol. The substance was thus obtained in colourless blades, melting constantly at 122°. The melting point thus coincides with that of the diphenyldimethyl*cyclo*pentenone already described, and the two substances are very similar in appearance; but a mixture of equal weights of the two was found to melt as low as 100—102°.

Analysis gave figures agreeing with the formula of a *diphenyldimethyl*cyclo*pentanone.*

0·1574 gave 0·4956 CO_2 and 0·1077 H_2O. C = 85·87; H = 7·60.
0·1908 „ 0·6014 CO_2 „ 0·1304 H_2O. C = 85·96; H = 7·59.
$C_{19}H_{20}O$ requires C = 86·36; H = 7·58 per cent.

The foregoing experiment was made with the object of preparing the hydrocarbon, diphenyldimethyl*cyclo*pentane; as both anhydracetonebenzil and the two methylanhydracetonebenzils yield, when boiled with hydriodic acid and red phosphorus, the corresponding *cyclo*pentanes; but in the present case the reduction appears not to proceed beyond the formation of the saturated cyclic ketone. The first stage of the reduction is, of course, the formation of diphenyldimethyl*cyclo*pentenone (m. p. 122°) as already described.

Diphenyldimethyl*cyclo*pentanone may be distilled under reduced pressure without decomposing.

By spontaneous evaporation of its solution in ethyl acetate, with the addition of light petroleum, it was obtained in six-sided, tabular crystals, showing straight extinction, having a sp. gr. of 1·1393 at 15°, and melting as above at 122°. Sometimes the crystals display a prismatic habit.

Happening to meet with (in an experiment to be described later on) certain crystals which behaved, on melting, like a mixture of diphenyldimethyl*cyclo*pentanone with the corresponding *cyclo*pentenone melting at 122°, we made a mixture of equal weights of these two compounds, dissolved it in ethyl acetate, and added light petroleum. The solution

deposited irregular crystals, melting at 100—102°, and having a sp. gr. of 1·1546 at 15°. This specific gravity is almost exactly the mean of those of the two constituent substances: namely, 1·1393 for the *cyclo*pentanone, and 1·1775 for the *cyclo*pentenone. One crystal, however, did not melt until 108°, showing that the proportion of the constituents in the mixed crystals is not invariable.

*Reduction of Diphenyldimethyl*cyclo*pentenone* (m. p. 122°).—A specimen of diphenyldimethyl*cyclo*pentenone (m. p. 122°), prepared by Vorländer and Wilcke's method (V. and W.'s "dibenzylidenediethyl ketone"), was boiled for 5 hours* with hydriodic acid (sp. gr. 1·7) and red phosphorus. Purified by the process already described, it gave six-sided, tabular crystals of *diphenyldimethyl*cyclo*pentanone*, melting at 122°. The crystals were further identified by their optical properties and sp. gr., and by the mixture melting-point test, employing for admixture a specimen of diphenyldimethyl*cyclo*pentanone prepared from $\alpha\beta$-dimethylanhydracetonebenzil. The mixture melted at 122°, whilst a mixture of the crystals with the unreduced diphenyldimethyl*cyclo*pentenone (m. p. 122°) melted as low as 110°.

Action of Hydriodic Acid on Diphenyldimethyltetrahydro-γ-pyrone.—Five grams of the finely-powdered γ-pyrone were boiled for 5 minutes with excess of fuming hydriodic acid (sp. gr. 1·96). The product, purified in the usual way, was obtained by crystallisation from ethyl acetate, with the addition of light petroleum, in six-sided, tabular crystals which, from their vague melting point—110—119°—sp. gr. 1·1695, and other properties were apparently mixed crystals of *diphenyldimethyl*cyclo*pentenone* and *diphenyldimethyl*cyclo*pentanone*, although, as the higher sp. gr. showed, containing a greater proportion of the former constituent than the mixed crystals already described. We were in fact able to prepare crystals of approximately the foregoing physical properties by allowing a mixture of 3 parts of diphenyldimethyl*cyclo*pentenone (m. p. 122°) with 1 part of diphenyldimethyl*cyclo*pentanone to crystallise from ethyl acetate with the addition of light petroleum. The separation of the constituents of such mixed crystals by crystallisation would be a very tedious process, if indeed it is at all feasible.

The reaction consists (1) in the transformation of the diphenyldimethyltetrahydro-γ-pyrone into diphenyldimethyl*cyclo*pentenone (m. p. 122°), the hydriodic acid playing the part of the hydrochloric acid in Vorländer and Wilcke's reaction (*loc. cit.*) for the preparation of the same compound; and (2) in the reduction of a portion of the *cyclo*pentenone to a *cyclo*pentanone, as in the reaction already

* In the earlier experiments, we boiled the various substances with the reducing mixture for five hours, but we afterwards found that boiling for a shorter period (one and a half hours) gave a better yield.

described. That this explanation is correct, is shown by the fact that, by the more protracted action of boiling hydriodic acid on diphenyldimethyltetrahydro-γ-pyrone, as described in the following experiment, only diphenyldimethyl*cyclo*pentanone is obtained.

Six grams of diphenyldimethyltetrahydro-γ-pyrone, 12 grams of red phosphorus, and 90 grams of hydriodic acid (sp. gr. 1·7) were boiled together for 5 hours. The product, purified in the usual way, was found to consist of *diphenyldimethyl*cyclo*pentanone.* After recrystallising it twice from alcohol, 3 grams of this compound, melting constantly at 122°, were obtained. It was identified by the mixture melting-point test, and by the form, optical properties, and specific gravity of the crystals deposited by spontaneous evaporation from its solution in ethyl acetate with addition of light petroleum.

*Oxime of Diphenyldimethyl*cyclo*pentanone.*—Two grams of diphenyldimethyl*cyclo*pentanone, 1·5 grams of hydroxylamine hydrochloride, and a sufficiency of absolute alcohol, were introduced into a flask fitted with a reflux condenser, and the mixture was boiled for 4 hours on the water-bath, adding 1·6 grams of anhydrous sodium carbonate in small quantities at a time. The liquid was filtered while hot, and water was added to the filtrate until a turbidity was produced. The crystals, which were gradually deposited, were recrystallised from alcohol. The substance was thus obtained in two forms: slender needles and minute laminæ. The melting point exhibits an anomaly: the substance generally melts at 158—159°, but after allowing it to cool and resolidify, does not melt until 165·5°. Sometimes crystals are obtained which show the higher melting point without previous fusion and resolidification; and these crystals induce the growth of their own kind in supersaturated solutions of the oxime. The substance is obviously dimorphous.

A nitrogen determination gave figures agreeing with the formula of the expected *oxime.*

0·2658 gave 11·4 c.c. moist nitrogen at 12° and 775 mm. N = 5·19.
$C_{19}H_{21}ON$ requires N = 5·02 per cent.

In another preparation, this substance, possibly owing to local superheating, was obtained in brownish crystals, which had to be decolorised by boiling their alcoholic solution with animal charcoal.

*Action of Bromine on Diphenyldimethyl*cyclo*pentanone.*—1·4 grams of diphenyldimethyl*cyclo*pentanone were dissolved in chloroform, 4 grams of bromine, also dissolved in chloroform, were added, and the mixture was left for 24 hours. Hydrogen bromide was evolved, and on expelling the chloroform and excess of bromine in a current of dry air, small, tabular crystals were deposited. The substance crystallises from benzene, on addition of methyl alcohol, in radiating groups of

needles or prisms. It also crystallises from light petroleum in small prisms, and from ether in needles. The crystals show oblique extinction. Heated slowly, the crystals melt at 179°, turning red and decomposing; but by plunging the capillary tube containing the substance into a bath already heated to 180°, and raising the temperature rapidly, the melting point 192° (with decomposition) was observed. The yield was 2 grams.

0·2749 gave 0·5442 CO_2 and 0·1070 H_2O. C = 53·99; H = 4·32.
0·1783 „ 0·1593 AgBr. Br = 38·02.
$C_{19}H_{18}OBr_2$ requires C = 54·03; H = 4·27; Br = 37·91 per cent.

The compound is therefore a *diphenyldimethyldibromocyclopentanone*, doubtless of the constitution $\begin{matrix} C_6H_5\cdot CH\cdot CBr(CH_3) \\ | \\ C_6H_5\cdot CH\cdot CBr(CH_3) \end{matrix}\!\!>CO.$

III. 4 : 5-*Diphenyl*-1 : 3-*dimethyl*cyclo*penten*(5)-*one*(2),

$$\begin{matrix} C_6H_5\cdot C{=\!=\!=}C(CH_3) \\ | \\ C_6H_5\cdot CH\cdot CH(CH_3) \end{matrix}\!\!>CO.$$

In preparing the diphenyldimethyltetrahydro-γ-pyrone used in the foregoing experiments, we had no very precise details of the method previously used to guide us. Vorländer and Hobohm (*Ber.*, 1896, **29**, 1352), who first prepared this compound, merely mention that it is obtained by the condensation of 2 mols. of benzaldehyde with 1 mol. of diethyl ketone in presence of alcohol and aqueous potassium hydroxide. On the other hand, the method described by Vorländer (*Annalen*, 1896, **294**, 296) for condensing these two substances is intended primarily to yield benzylidenediethyl ketone, the γ-pyrone derivative being obtained only as a by-product. We gather, however, from the description there given, that, in the experiment about to be described, we probably used a considerably stronger solution of potassium hydroxide than was employed by Vorländer and Hobohm—a circumstance which doubtless accounts for our obtaining, along with the γ-pyrone derivative, a substance not observed by our predecessors in this work.

One hundred and twenty grams of benzaldehyde, 40 grams of diethyl ketone, 300 c.c. of absolute alcohol, 250 c.c. of water, and 10 c.c. of a 33·3 per cent. solution of potassium hydroxide were mixed in a stout bottle; the mixture, which was clear at first, speedily became turbid and in a short time separated into two layers, indicating the occurrence of the first stage of the condensation. Fifty grams of solid potassium hydroxide were then added in successive portions of 10 grams each, shaking after each addition, until everything had gone into solution, before adding the next portion. The whole was then

mechanically shaken until the organic substance had become quite pasty, which required about 4½ days. The product was separated by filtration, pressed, and dissolved in boiling methyl alcohol. As the solution cooled, prismatic crystals of diphenyldimethyltetrahydro-γ-pyrone * separated. The mother liquor was decanted from these while the solution was still warm, in order to prevent a second substance, melting at 128°, which, as we had ascertained from a previous experiment, is formed at the same time, from crystallising out. The yield of almost pure γ-pyrone derivative thus obtained was 41 grams, and more was separated from the mother liquor. The decanted solution, on further cooling, deposited a second substance crystallising in large, serrated blades, mixed, however, with diphenyldimethyltetrahydro-γ-pyrone. The new compound was purified by fractional crystallisation from methyl alcohol or ethyl alcohol, in which it is much less soluble than the γ-pyrone derivative. It melted, as already stated, at 128°. It is formed in relatively small quantity, which accounts for its remaining, in spite of its more sparing solubility, in the first mother liquor.

0·1661 gave 0·5276 CO_2 and 0·1034 H_2O. C = 86·62 ; H = 6·91.
0·1766 ,, 0·5626 CO_2 ,, 0·1094 H_2O. C = 86·88 ; H = 6·88.
$C_{19}H_{18}O$ requires C = 87·02 ; H = 6·87 per cent.

The reactions of this compound show that it is 4 : 5-*diphenyl*-1 : 3-*dimethyl*cyclo*penten*(5)-*one*(2), as formulated at the head of the present section of this paper.

A portion of the compound was distilled under a pressure of 12 mm. The distillate consisted of a small quantity of needle-shaped crystals embedded in a vitreous matrix. On crystallising from alcohol, needles were obtained (m. p. about 257°) in quantity too small for further examination. The greater portion of the distillate was an uncrystallisable gum.

The compound, therefore, decomposes when distilled. For this reason Vorländer and Hobohm would not have been able to detect the presence of this substance, even had it been formed in their reaction, as they purified their crude diphenyldimethyltetrahydro-γ-pyrone by distillation.

Transformation of Diphenyldimethyltetrahydro-γ-pyrone into 4 : 5-*Diphenyl*-1 : 3-*dimethylpenten*(5)-*one*(2).—Our suspicion that the formation of the diphenyldimethyl*cyclo*pentenone melting at 128° was due to the

* The melting point of diphenyldimethyltetrahydro-γ-pyrone is given by Vorländer and Hobohm (*loc. cit.*) at 106°. M. M. Richter ("Lexikon") gives, in addition, the melting point 109°, the authority for which we have not been able to trace. We find that the substance, when sufficiently purified by recrystallisation from methyl alcohol, melts constantly at 111·5—112·5°.

action of the relatively strong solution of potassium hydroxide on diphenyldimethyltetrahydro-γ-pyrone primarily formed, was confirmed by the following experiment, in which, by using a still stronger solution of alkali, the transformation is complete.

To a solution of 75 grams of potassium hydroxide in 300 grams of absolute alcohol, 24 grams of the finely-powdered pyrone were added, and the mixture was mechanically shaken for a week, after which it was left for another week, shaking it from time to time. The appearance of the undissolved substance had totally changed: the liquid was filled with glistening laminæ. The product, separated by filtration, weighed 10·5 grams. By recrystallisation from boiling alcohol, it was separated into two substances: pink-coloured laminæ melting at 128°, and needles melting at 265°, the latter compound being obtained in quantity too small for further examination. By recrystallisation from methyl alcohol, the plates were obtained colourless and melted as before at 128°. The substance was identical with the 4 : 5-*diphenyl*-1 : 3-*dimethyl*cyclo*penten*(5)-*one*(2) just described, as was proved by the mixture melting-point test.

We also examined the action of strong alcoholic potassium hydroxide in the cold on diphenyltetrahydro-γ-pyrone (previously prepared by Petrenko-Kritschenko and Plotnikoff, *Ber.*, 1897, **30**, 2802), in the hope of obtaining a diphenyl*cyclo*pentenone isomeric with that which is formed by the reduction of anhydracetonebenzil; but as the product of the reaction was amorphous, we did not further investigate it.

*Behaviour of the Isomeric Diphenyldimethyl*cyclo*pentenones towards Potassium Permanganate.*—Alcoholic solutions of the two diphenyldimethyl*cyclo*pentenones (m. p. 122° and m. p. 128°) were prepared, a few drops of sodium carbonate solution were added to each, and then a drop of a solution of potassium permanganate. In the case of the compound melting at 122°, the mixture required 15 minutes to turn brown; with the isomeride melting at 128°, the change occurred immediately.

This difference in behaviour indicates, in the first place, that the two compounds differ in their structure, and are not merely stereoisomeric. There are only two formulæ possible for structurally isomeric diphenyldimethyl*cyclo*pentenones containing the methyl and phenyl groups in the positions in which they are present in these compounds; and we would assign these as follows to the two compounds:

$$\left.\begin{array}{l} C_6H_5\cdot C\cdot CH(CH_3) \\ \quad\;\; \| \\ C_6H_5\cdot C\cdot CH(CH_3) \end{array}\right>CO \qquad \left.\begin{array}{l} C_6H_5\cdot C{=\!=}C(CH_3) \\ \quad\;\; | \\ C_6H_5\cdot CH\cdot CH(CH_3) \end{array}\right>CO.$$

Isomeride melting at 122°. Isomeride melting at 128°.

The first formula explains the greater stability of the compound

towards permanganate, inasmuch as compounds containing the group $C_6H_5\cdot\overset{|}{C}:\overset{|}{C}\cdot C_6H_5$, in which no hydrogen is attached to the ethylene complex, are specially stable towards permanganate; thus, diphenylmaleic acid dissolved in sodium carbonate does not reduce permanganate in the cold. This first formula, moreover, is in keeping, as has been already mentioned, with the formation of the compound by the reduction of $\alpha\beta$-dimethylanhydracetonebenzil with hydriodic acid. These formulæ also account for the behaviour of the respective compounds with bromine and towards reducing agents.

Oxime of 4 : 5-*Diphenyl*-1 : 3-*dimethyl*cyclo*penten*(5)-*one*(2). — The diphenyldimethyl*cyclo*pentenone melting at 128° was converted into its oxime by the process already described in the case of the corresponding *cyclo*pentanone. The product was purified by recrystallisation, first from ethyl alcohol, then from methyl alcohol, and finally from light petroleum. It was thus obtained in short, flat needles, which soften at 115° and melt at 121·5°.

A nitrogen determination gave a value agreeing with that required for the expected *oxime*.

0·2245 gave 10·05 c.c. moist nitrogen at 11° and 757 mm. N = 5·31

$C_{19}H_{19}ON$ requires N = 5·05 per cent.

Action of Bromine on 4 : 5-*Diphenyl*-1 : 3-*dimethyl*cyclo*penten*(5)-*one*(2).—One gram of the diphenyldimethyl*cyclo*pentenone melting at 128° was dissolved in chloroform, and to the cold solution 2·5 grams of bromine, also dissolved in chloroform, were added. Heat was evolved, but no hydrogen bromide was given off. The mixture was left for 24 hours, after which the solvent and the excess of bromine were expelled in a current of dry air. The resulting crystalline product weighed 1·8 grams. It was recrystallised once from ethyl alcohol and twice from benzene with the addition of methyl alcohol. It was deposited from the latter solvent in radiating groups of prisms or needles melting at 185° with decomposition. The best crystals were obtained from light petroleum. They showed straight extinction.

0·2940 gave 0·5820 CO_2 and 0·1144 H_2O. C = 53·99 ; H = 4·32.
0·2212 „ 0·1973 AgBr. Br = 37·96.
$C_{19}H_{18}OBr_2$ requires C = 54·03 ; H = 4·27 ; Br = 37·91 per cent.

The compound is therefore the additive *dibromide*,

$$\begin{array}{l} C_6H_5\cdot CBr\cdot CBr(CH_3) \\ \quad\quad\;\; | \\ C_6H_5\cdot CH-CH(CH_3) \end{array}\!\!>\!CO,$$

and the addition of bromine is not accompanied by substitution as it is in the case of the isomeric diphenyldimethyl*cyclo*pentanone melting at 122°. It is isomeric with the compound obtained by bromina-

ting diphenyldimethyl*cyclo*pentanone. The melting points of the two compounds are too indefinite and too close together to serve as a criterion, and the crystalline forms are very similar; but the optical properties of the two kinds of crystals (*v. supra*) distinguish sharply between them.

Action of Hydriodic Acid.—One gram of the diphenyldimethyl*cyclo*pentenone melting at 128°, 2 grams of red phosphorus, and 15 grams of hydriodic acid (sp. gr. 1·7) were boiled for 4 hours. The product, purified in the usual way, was deposited from alcohol in elongated plates melting at 122°. The specific gravity, the form, and the optical properties of the crystals were those of *diphenyldimethyl*cyclo*pentanone*, and the identity of the compound was established by the mixture melting-point test. On the other hand, when the substance was mixed with a specimen of the diphenyldimethyl*cyclo*pentenone melting at 122°, the melting point was considerably depressed.

The result of the foregoing reduction shows that the compound melting at 128° contains the *cyclo*pentenone group.

Action of Alcoholic Hydrochloric Acid.—Half a gram of the diphenyldimethyl*cyclo*pentenone melting at 128° was dissolved in absolute alcohol, 20 drops of a saturated alcoholic solution of hydrochloric acid were added, and the whole was heated on the water-bath for 1 hour. The solution, which had become concentrated, deposited, on cooling, needle-shaped crystals of a substance melting at about 260°, the quantity of which was too small for further examination. The mother liquor, when further evaporated, yielded six-sided plates of a substance, which, after recrystallisation from alcohol and subsequently from ethyl acetate, with addition of light petroleum, was obtained in the characteristic forms of 4 : 5-*diphenyl*-1 : 3-*dimethyl*cyclo*penten*(4)-*one*(2),

$$\begin{array}{l} C_6H_5\cdot C\cdot CH(CH_3) \\ \quad\quad\ \ \| \\ C_6H_5\cdot C\cdot CH(CH_3) \end{array}\!\!>CO,$$

with an extinction angle of 34° and melting at 122°. The mixture melting-point test, in which we employed for admixture a specimen of this compound prepared by the reduction of *aβ*-dimethylanhydracetonebenzil, gave no depression.

Under the influence of hydrochloric acid, therefore, the position of the double bonds is shifted from the 1 : 5- to the 4 : 5-position, and the diphenyldimethyl*cyclo*pentenone melting at 128° is transformed into its isomeride melting at 122°.

It is possible therefore that, in the reduction of the diphenyldimethyl*cyclo*pentenone (m. p. 128°) with hydriodic acid and red phosphorus, the foregoing transformation, occurring under the influence of the acid, precedes the reduction.

IV. *Two Isomeric Compounds of the Formula* $C_{18}H_{18}O_2$, *obtained by the Condensation of Benzaldehyde with Methyl Ethyl Ketone.*

We determined to prepare diphenylmethyltetrahydro-γ-pyrone in order to ascertain whether it could be converted into compounds containing the pentacarbon ring. Two methods were available for the preparation of this substance: that of Levinstein (*Inaugural-Diss.*, Berlin, 1902) and that of Harries and Müller (*Ber.*, 1902, **35**, 968).

Levinstein obtained the compound by the condensation of benzaldehyde with methyl ethyl ketone under the influence of sodium hydroxide. We carried out the process as follows, and as our results differ from those of our predecessors, we will describe the procedure in detail.

One hundred and twenty grams of benzaldehyde, 33 grams of methyl ethyl ketone, 200 c.c. of alcohol, 480 c.c. of water, and 33 grams of a 10 per cent. aqueous solution of sodium hydroxide were mixed, and the mixture was mechanically shaken for a week. The pasty mass of organic substance was dissolved in ether and, after drying the ethereal solution with calcium chloride, the ether was expelled and the residue distilled under about 12 mm. pressure. The following fractions were collected:

1. Up to 140°. Mainly benzaldehyde.
2. 140—200°. Solidified almost immediately, and consisted chiefly of α-benzylidenemethyl ethyl ketone.
3. 200—250°. Viscid oil.

Fraction 3 was redistilled, and the chief sub-fraction, which passed over between 220° and 240° (12 mm. pressure), was dissolved in boiling methyl alcohol. A crop of crystals weighing 15·5 grams was obtained, but the substance was evidently a mixture. It was redissolved in boiling light petroleum (b. p. 80—100°), which deposited it in two forms: plates, and tufts of needles. By mechanical separation and recrystallisation of the separated products from methyl alcohol, the two compounds were obtained in sufficient quantity to serve as nuclei in the subsequent process of fractional crystallisation. The remainder of the mixture was dissolved in boiling light petroleum, and the crystallisation was started with one of the substances, separating the crop by filtration before the solution was cold. The crystallisation of the filtrate, after previous concentration, was started with the second substance. Finally, the separated substances were recrystallised from methyl alcohol until they showed constant melting points. We thus obtained (1) large six-sided plates melting at 82—83°; (2) long rectangular plates melting at 102—103°. Both compounds gave, on analysis, figures agreeing with the formula $C_{18}H_{18}O_2$.

Compound melting at 82—83°.

0·1100 gave 0·5359 CO_2 and 0·1804 H_2O. C = 81·02 ; H = 6·75
$C_{18}H_{18}O_2$ requires C = 81·23 ; H = 6·77 per cent.

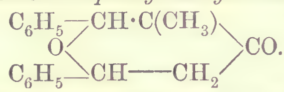
Compound melting at 102—103°.

0·1731 gave 0·5157 CO_2 and 0·1071 H_2O. C = 81·25 ; H = 6·87
0·1878 „ 0·5622 CO_2 „ 0·1148 H_2O. C = 81·64 ; H = 6·79
$C_{18}H_{18}O_2$ requires C = 81·23 ; H = 6·77 per cent.

The compounds are formed according to the equation

$$2C_6H_5{\cdot}CHO + CH_3{\cdot}CO{\cdot}C_2H_5 = C_{18}H_{18}O_2 + H_2O,$$

and might be stereoisomeric *diphenylmethyltetrahydro-γ-pyrones*,



We also employed Harries and Müller's method of preparation (*loc. cit.*) by shaking a mixture of α-benzylidenemethyl ethyl ketone and benzaldehyde with an aqueous-alcoholic solution of sodium hydroxide, but obtained the same two compounds melting respectively at 82—83° and 102—103°. This experiment disposes of the possible objection that one or both of these compounds might have been formed from an impurity in the methyl ethyl ketone which we employed.

Levinstein gives the melting point of his condensation compound $C_{18}H_{18}O_2$ as 74° ; Harries and Müller give 68·5° for theirs. As already mentioned, we suspect that these investigators were dealing with mixtures of the two compounds just described.

We studied the action of hot alcoholic hydrogen chloride on both these compounds, and of hydriodic acid at its boiling point, and of alcoholic potassium hydroxide in the cold, on the compound melting at 102—103°, but did not succeed in isolating anything definite from the products of the reactions.

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Interaction of Sodium Phenylglycidate with Phenylhydrazine.

By Francis Robert Japp, F.R.S., and William Maitland, B.Sc., Carnegie Fellow in the University of Aberdeen.

The action of hydrazines on compounds containing the ethylene oxide group ("$\alpha\beta$-oxido-compounds"—compare Japp and Michie, Trans., 1903, **83**, 281, footnote) has been relatively little studied.

By the action of hydrazine on ethylene oxide, Knorr and Brownsdon (*Ber.*, 1902, **35**, 4474) obtained *as*-diethanolhydrazine,

$$NH_2\cdot N(CH_2\cdot CH_2\cdot OH)_2,$$

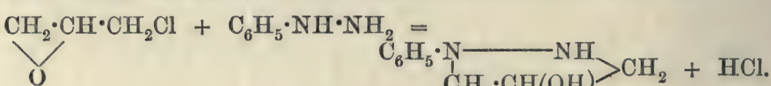
which, by dehydration, yielded a small quantity of morpholylhydrazine along with a considerable amount of morpholine.

A more complex case had been previously studied by Balbiano in the action of epichlorhydrin on hydrazines. By heating epichlorhydrin with twice its molecular proportion of phenylhydrazine, a mixture of 1-phenylpyrazole, aniline and ammonium chloride was obtained:

$$C_3H_5OCl + 2C_6H_5\cdot NH\cdot NH_2 = C_3H_5O\cdot N_2H_2\cdot C_6H_5 + C_6H_5\cdot NH\cdot NH_2,HCl = C_6H_5\cdot NH_2 + NH_4Cl + H_2O + C_3H_3N_2\cdot C_6H_5$$

(*Gazzetta*, **17**, 176).

The intermediate compound $C_9H_{12}ON_2$, the formation of which was assumed by Balbiano, was obtained by F. Gerhard (*Ber.*, 1891, **24**, 352) by the interaction of epichlorhydrin and phenylhydrazine at the ordinary temperature. He explains its formation as follows:



Such a compound would be 1-phenyl-4-hydroxytetrahydropyrazole. It yields a monacetyl derivative and, when heated with phenylhydrazine hydrochloride, is converted into 1-phenylpyrazole as in Balbiano's second equation.

Japp and Michie (Trans., 1903, **83**, 283, 284 and 286) showed that both acetodiphenylmethyloxidobutyric acid and diphenyldimethyloxidoglutaric acid give, with phenylhydrazine, reactions somewhat similar to the foregoing, the oxido-group of the acid interacting additively with the basic imino-group of the phenylhydrazine, and the resulting compound parting with water to form, in the case of the first acid, a pyrazolidone ring and, in that of the second, both a pyrazolidone and a furfuran ring (compare *loc. cit.*).

Owing to the complexity of the compounds formed in these two cases, it seemed desirable to study the reaction with an oxido-compound of a simpler character, and in this way to prepare, if possible, some substance of already known constitution, so as to test the validity of the interpretation put upon the reaction by Japp and Michie. We selected for this purpose phenylglycidic acid (β-phenyl-$\alpha\beta$-oxido-propionic acid), which, on account of the instability of the free acid, we employed in the form of its sodium salt. The reaction was further of interest because Erlenmeyer, jun. (*Annalen*, 1892, 271, 167), in comparing the reactions of phenylpyruvic acid with those of the isomeric phenylglycidic acid, shows that the former compound interacts with phenylhydrazine, but he apparently takes for granted that phenylglycidic acid will not do so. Had he tried the experiment he would have found that both acids interact with phenylhydrazine according to the equation:

$$C_9H_8O_3 + C_6H_5\cdot NH\cdot NH_2 = C_{15}H_{14}O_2N_2 + H_2O,$$

the resulting compounds, however, being quite distinct.

We find, therefore, that when phenylglycidic acid, in the form of its sodium salt, is heated with phenylhydrazine in alcoholic solution, these substances interact, yielding 1 : 5-*diphenyl-4-hydroxy-3-pyrazolidone*,

$$C_6H_5\cdot\underbrace{CH\cdot CH}_{O}\cdot CO_2H + C_6H_5\cdot NH\cdot NH_2 = \begin{array}{l} C_6H_5\cdot N\text{———}NH \\ C_6H_5\cdot CH\cdot CH(OH) \end{array}\Big>CO + H_2O,$$

this compound being obtained in the form of its sodium salt, which, when recrystallised from water, has the formula $C_{15}H_{13}O_2N_2Na,4H_2O$. The pyrazolidone, liberated by acids, dissolves in sodium carbonate, regenerating this salt. It yields a *diacetyl* derivative,

$$\begin{array}{l} C_6H_5\cdot N\text{———}N(C_2H_3O) \\ C_6H_5\cdot CH\cdot CH(O\cdot C_2H_3O) \end{array}\Big>CO.$$

By heating the sodium salt of the pyrazolidone with methyl iodide, the *methyl* derivative, $\begin{array}{l} C_6H_5\cdot N\text{—}N(CH_3) \\ C_6H_5\cdot CH\cdot CH(OH) \end{array}\Big>CO$, is obtained, which has no acid properties, is not hydrolysed by sodium hydroxide, and yields a *monacetyl* derivative.

By distilling the pyrazolidone under reduced pressure, or, better, by fusing it with zinc chloride, or by warming it for some hours with a solution of potassium hydroxide or sodium carbonate, it parts with water and is converted into 1 : 5-*diphenyl-3-pyrazolone*,

$$\begin{array}{l} C_6H_5\cdot N\cdot NH \\ C_6H_5\cdot C\cdot CH \end{array}\Big>CO$$

(m. p. 252°), previously obtained by Knorr (*Ber.*, 1887, 20, 1107) by distilling *cinnamoylphenylhydrazine*:

$$C_6H_5\cdot CH:CH\cdot CO\cdot NH\cdot NH\cdot C_6H_5 = \begin{matrix} C_6H_5\cdot N\cdot NH \\ C_6H_5\cdot C:CH \end{matrix}\!\!>CO + H_2.$$

This diphenylpyrazolone yields a *monacetyl* derivative.

The compound which we have formulated as a diphenylhydroxypyrazolidone is not reduced by sodium in boiling alcoholic solution, is not oxidised by Fehling's solution, and does not interact with benzaldehyde even at the boiling point of the latter substance. These negative results, taken in conjunction with the facts that the compound forms a diacetyl derivative and also a methyl derivative which is insoluble in and not hydrolysable by alkalis, exclude the constitutional formula $\begin{matrix} C_6H_5\cdot C:CH\cdot CO_2H \\ N(C_6H_5)\cdot NH_2 \end{matrix}$, which might otherwise call for consideration.

We found that sodium phenylglycidate also interacted with hydrazine hydrate and with β-naphthylhydrazine, but as we were unable to obtain the products in a crystallised condition, we did not investigate them further.

Experimental.

Action of Phenylhydrazine on Sodium Phenylglycidate: Formation of 1:5-*Diphenyl-4-hydroxy-3-pyrazolidone.*—Ten grams of sodium phenylglycidate, 10 grams of phenylhydrazine and 50 c.c. of alcohol were introduced into a tube, which was then exhausted, sealed up, and heated for 9 hours at 100° in a water-bath. During the earlier part of the heating, the tube was shaken from time to time, until the whole of the sodium phenylglycidate had dissolved. On allowing the contents of the tube to cool and diluting with alcohol, a crystalline sodium salt separated, the amount of which increased on standing. This was filtered off, washed with cold alcohol, ground with ether, again filtered, and washed with ether. The yield of salt, thus treated, was 13 grams. On dissolving a portion of this salt in water and acidifying with dilute sulphuric acid, an organic substance was precipitated. The organic compound crystallised from alcohol in rectangular laminæ, and from benzene in needles, melting at 173·5°.

0·1553 gave 0·4021 CO_2 and 0·0813 H_2O. C = 70·61; H = 5·82.
0·1624 „ 15·0 c.c. moist nitrogen at 10° and 755 mm. N = 10·99.
$C_{15}H_{14}O_2N_2$ requires C = 70·86; H = 5·51; N = 11·02 per cent.

This is the composition of 1:5-*diphenyl-4-hydroxy-3-pyrazolidone*,

$$\begin{matrix} C_6H_5\cdot N \text{———} NH \\ C_6H_5\cdot CH\cdot CH(OH) \end{matrix} \!\!>\! CO,$$ a constitution to which the reactions of this substance point.

A portion of the foregoing sodium salt was recrystallised twice from water, from which it was deposited in indistinct needle-shaped crystals. It became pink-coloured in the process. Analysis gave figures agreeing with the formula $C_{15}H_{13}O_2N_2Na,4H_2O$.

0·4050 lost, at 80°, 0·0822. $H_2O = 20·30$.
$C_{15}H_{13}O_2N_2Na,4H_2O$ requires $H_2O = 20·69$ per cent.
0·3228 anhydrous salt gave 0·0828 Na_2SO_4. Na = 8·31.
$C_{15}H_{13}O_2N_2Na$ requires Na = 8·33 per cent.

The weight of the salt dried at 80° is practically constant. A very little above that temperature the substance begins to decompose. The salt crystallises from hot alcohol in tufts of needles.

The pyrazolidone dissolves in a hot solution of sodium carbonate. On cooling, the liquid deposits the foregoing salt. The heating with the sodium carbonate solution should not be continued longer than is necessary to dissolve the substance, otherwise dehydration of the product occurs, and 1 : 5-diphenyl-3-pyrazolone is formed (*v. infra*).

The pyrazolidone can be titrated, although not quite accurately, with sodium hydroxide in alcoholic solution, using phenolphthalein as an indicator. Thus 1 gram of the pyrazolidone required 0·1549 gram NaOH for neutralisation; the calculated value being 0·1575 gram NaOH, on the assumption that $C_{15}H_{14}O_2N_2$ behaves like a monobasic acid.

Diacetyl Derivative of Diphenylhydroxypyrazolidone,

$$\begin{matrix} C_6H_5\cdot N \text{———} N(C_2H_3O) \\ C_6H_5\cdot CH\cdot CH(O\cdot C_2H_3O) \end{matrix} \!\!>\! CO.$$

—The pyrazolidone was boiled with 10 times its weight of acetic anhydride for $6\frac{1}{2}$ hours, the excess of anhydride was distilled off under reduced pressure, and the residue was recrystallised from alcohol. It formed short needles, melting constantly at 152°.

0·1516 gave 0·3726 CO_2 and 0·0746 H_2O. C = 67·03; H = 5·47.
0·1757 „ 12·5 c.c. moist nitrogen at 12° and 761 mm. N = 8·45.
$C_{19}H_{18}O_4N_2$ requires C = 67·45; H = 5·33; N = 8·28 per cent.

When the diacetyl derivative is digested on the water-bath with a solution of sodium carbonate, it dissolves very slowly. In the process it is hydrolysed, but the resulting diphenylhydroxypyrazolidone is dehydrated by the long digestion, yielding 1 : 5-*diphenyl-3-pyrazolone* (*v. infra*). This substance was precipitated by acidifying with acetic acid. It crystallised from alcohol in needles melting at 252°, and was further identified by the mixture melting-point test.

Warming for some time with dilute alcoholic sodium hydroxide produces the same change.

1 : 5-*Diphenyl-2-methyl-4-hydroxy-3-pyrazolidone*,

$$\begin{matrix} C_6H_5\cdot N & \!\!\!\!-\!\!-\!\!-\; N(CH_3) \\ C_6H_5\cdot CH & \!\!\!\!\cdot CH(OH) \end{matrix} > CO.$$

—A quantity of the sodium salt of diphenylhydroxypyrazolidone was boiled with a slight excess of methyl iodide in methyl-alcoholic solution for $3\frac{1}{2}$ hours. On pouring the product into water an oil separated, which soon solidified. A further quantity of the same substance was obtained by extracting the aqueous-alcoholic mother liquor with ether. By washing the product with a little ether and recrystallising from hot alcohol, the substance was obtained in six-sided crystals, sometimes elongated, or even lath-shaped, melting at 163—164°. It is slightly soluble in water.

0·1860 gave 0·4861 CO_2 and 0·1015 H_2O. C = 71·27 ; H = 6·06.
0·1533 „ 13·55 c.c. moist nitrogen at 10° and 756·5 mm. N = 10·54.
$C_{16}H_{16}O_2N_2$ requires C = 71·64 ; H = 5·97 ; N = 10·45 per cent.

The substance is thus a *methyl* derivative of diphenylhydroxypyrazolidone.

As it appeared to be slightly more soluble in aqueous sodium hydroxide than in water, we were at first inclined to credit it with acid properties. A titration experiment, however, showed that it does not interact with the alkali. A small quantity of the substance (0·3272 gram) was dissolved in alcohol with phenolphthalein as an indicator, and 0·2 c.c. of an alcoholic solution of sodium hydroxide (4·87 NaOH per litre) was added. The lavender coloration which phenolphthalein gives with alkaline hydroxides in strong alcohol was at once produced, and did not disappear either on standing or on warming. The methyl derivative, therefore, unlike the parent substance, cannot be titrated under the foregoing conditions, nor is it hydrolysed by the alkali. These results indicate that the methyl group is attached to nitrogen and not to oxygen, and that the compound is therefore 1 : 5-*diphenyl-2-methyl-4-hydroxy-3-pyrazolidone.*

By protracted warming with aqueous sodium hydroxide on the water-bath, the compound was totally decomposed.

Attempts to dehydrate the methyl derivative to a diphenylmethylpyrazolone, either by distilling it under reduced pressure or by heating it with zinc chloride—methods, which, as will be seen later on, gave positive results in the case of diphenylhydroxypyrazolidone—were unavailing. In both cases only unchanged substance was recovered.

Acetyl Derivative, $\begin{matrix} C_6H_5\cdot N & \!\!\!\!-\!\!-\!\!-\!\!-\!\!-\; N(CH_3) \\ C_6H_5\cdot CH & \!\!\!\!\cdot CH(O\cdot C_2H_3O) \end{matrix} > CO.$—The methyl derivative was acetylated with acetic anhydride, as described in the case

of the pyrazolidone, boiling for 3 hours. The product crystallised from alcohol in obliquely-terminated, flat prisms, or in oblique plates with bevelled edges, melting at 155°. Analysis showed that a *monacetyl* derivative had been formed.

0·1556 gave 0·3946 CO_2 and 0·0831 H_2O. C = 69·16; H = 5·93.
0·1695 „ 13·6 c.c. moist nitrogen at 18° and 759·5 mm. N = 9·26.
$C_{18}H_{18}O_3N_2$ requires C = 69·68; H = 5·81; N = 9·03 per cent.

Dehydration of 1 : 5-*Diphenyl*-4-*hydroxy*-3-*pyrazolidone: Formation of* 1 : 5-*Diphenyl*-3-*pyrazolone*, $\begin{matrix} C_6H_5\cdot N\cdot NH \\ C_6H_5\cdot C{=}CH \end{matrix}\!\!>\!CO$ (m. p. 252°).—One gram of diphenylhydroxypyrazolidone was heated in an Anschütz flask (a distilling flask with the receiver fused on to the tubulure) which was kept exhausted during the process by means of a Sprengel mercury pump. A reaction took place when the temperature of the oil-bath reached 230°, and the temperature was ultimately raised to 285°. Needle-shaped crystals condensed in the neck of the flask; these were twice recrystallised from glacial acetic acid, after which they melted constantly at 252°, and were found to be 1 : 5-*diphenyl*-3-*pyrazolone* formed by abstraction of the elements of 1 mol. of water from diphenylhydroxypyrazolidone. For comparison a specimen of the compound was prepared by Knorr's method (*Ber*., 1887, 20, 1107) of distilling cinnamoylphenylhydrazine. The two specimens were indistinguishable from one another; both melted at 252°, and there was no depression of melting point on mixing the two. A nitrogen determination confirmed this result.

0·1207 gave 12·0 c.c. moist nitrogen at 13° and 763 mm. N = 11·79.
$C_{15}H_{12}ON_2$ requires N = 11·86 per cent.

Gas was given off in the foregoing reaction, a resinous mass remained behind in the flask, and the yield of purified diphenylpyrazolone was only one-fifth of the weight of substance taken.

We afterwards discovered various other means of dehydrating diphenylhydroxypyrazolidone which gave much better yields of diphenylpyrazolone.

Thus diphenylhydroxypyrazolidone was mixed with solid zinc chloride and a few drops of water, and the mixture heated in a test-tube until the water was driven off and a clear yellow fused mass was produced. On dissolving the cooled mass in hot alcohol to which a few drops of acetic acid had been added, a solution was obtained which, on cooling, deposited an excellent yield of the diphenylpyrazolone (m. p. 252°).

Also by dissolving diphenylhydroxypyrazolidone in 8 per cent. aqueous potassium hydroxide, or even in sodium carbonate solution,

and heating on the water-bath at 100° for 2—4 hours, a solution is obtained which, on acidifying, gives diphenylpyrazolone. The yield is again good.

In an experiment in which we tried to reduce diphenylhydroxypyrazolidone by heating it on the water-bath with tin and aqueous-alcoholic hydrochloric acid, it was found that the compound had merely been dehydrated, yielding the foregoing diphenylpyrazolone.

As, by these various reactions, we had come into possession of a few grams of 1 : 5-diphenyl-3-pyrazolone, we studied some of the reactions of this substance. It is soluble in aqueous potassium hydroxide and is precipitated from the solution by carbon dioxide. An attempt to titrate the pyrazole in alcoholic solution with alcoholic sodium hydroxide, using phenolphthalein as an indicator, gave, however, a very unsatisfactory result, as only about three-quarters of the theoretical amount of sodium hydroxide was neutralised by the pyrazole, assuming that the latter acts as a monobasic acid.

2-*Acetyl*-1:5-*diphenyl-3-pyrazole*, $\begin{matrix} C_6H_5\cdot N\cdot N(C_2H_3O) \\ C_6H_5\cdot C\!=\!=\!=\!=\!CH \end{matrix}\!\!>\!CO$.—Diphenylpyrazole (m. p. 252°) was boiled for 4 hours with 10 times its weight of acetic anhydride. On distilling off the excess of anhydride under reduced pressure, a gum was left; on dissolving this in light petroleum, the solution, by spontaneous evaporation, deposited four-sided prisms, or thick, rhombic plates, melting constantly at 65—66°. A nitrogen determination showed that a *monacetyl* derivative had been formed.

0·1489 gave 12·8 c.c. moist nitrogen at 19° and 772 mm. N = 10·0.
$C_{17}H_{14}O_2N_2$ requires N = 10·07 per cent.

CHEMICAL DEPARTMENT,
UNIVERSITY OF ABERDEEN.

a-Benzoyl-β-trimethacetylstyrene.

By Francis Robert Japp, F.R.S., and William Maitland, B.Sc., Carnegie Fellow in the University of Aberdeen.

Japp and Klingemann (Trans., 1890, 57, 662) studied the peculiar transformations which $\alpha\beta$-dibenzoylstyrene (*αβ-dibenzoylcinnamene*—compare Trans., 1901, 79, 1013, footnote) undergoes under the influence of heat and of various chemical agents—transformations frequently involving the migration of a phenyl group. They were, moreover, able to show that these reactions were in almost every instance analogous to those of Zinin's "acicular oxylepiden" (dibenzoylstilbene), and in this way they succeeded in clearing up the constitution of the majority of the derivatives prepared by the latter investigator from this substance. The relation of the two compounds to one another is shown by the formulæ

$$\begin{array}{c} C_6H_5\cdot C{=}CH \\ C_6H_5\cdot CO\ \ CO\cdot C_6H_5 \end{array} \qquad\qquad \begin{array}{c} C_6H_5\cdot C{=}C\cdot C_6H_5 \\ C_6H_5\cdot CO\ \ CO\cdot C_6H_5 \end{array}$$

$\alpha\beta$-Dibenzoylstyrene (m. p. 129°). Dibenzoylstilbene (m. p. 220°).*

It seemed of interest to prepare some further representative of this class of unsaturated γ-diketones in order to ascertain whether it would exhibit similar reactions.

$\alpha\beta$-Dibenzoylstyrene is obtained by the condensation of benzil with acetophenone under the influence of potassium hydroxide. By substituting methyl *tert.*-butyl ketone for acetophenone in this reaction, we were able to prepare *α-benzoyl-β-trimethacetylstyrene* (m. p. 115°) according to the equation,

$$\begin{array}{c} C_6H_5\cdot CO \\ C_6H_5\cdot CO \end{array} + CH_3\cdot CO\cdot C(CH_3)_3 = \begin{array}{c} C_6H_5\cdot C{=}CH \\ C_6H_5\cdot CO\ \ CO\cdot C(CH_3)_3 \end{array} + H_2O.$$

In order that an unsaturated γ-diketone may with certainty be formed by the condensation of benzil with a ketone, it is necessary that one of the radicles of the ketone should be a primary alkyl and the other either a tertiary alkyl or an aryl. Unless this second condition is fulfilled, a closed-chain compound—a derivative of anhydracetonebenzil—will generally result. Thus benzil and methyl *iso*propyl ketone yield $\beta\beta$-di-

* Both of these compounds, as will be shown in a paper to be published shortly by one of us in conjunction with Mr. James Wood, have the *cis*-configuration.

methylanhydracetonebenzil, $\begin{array}{l} C_6H_5\cdot C\!=\!\!=\!\!=\!\!=\!\!=\!\!=CH \\ C_6H_5\cdot C(OH)\cdot C(CH_3)_2 \end{array}\!\!>\!CO$ (Japp and Meldrum, Trans., 1901, 79, 1037).

As the reactions of benzoyltrimethacetylstyrene for the most part run parallel with those of dibenzoylstyrene and dibenzoylstilbene, we will not, in the individual cases, call further attention to this parallelism, but will restrict ourselves to indicating where the reactions deviate in character from those previously described. The parallel reactions of dibenzoylstyrene and dibenzoylstilbene are given in the paper by Japp and Klingemann already quoted.

Benzoyltrimethacetylstyrene is readily converted into furfuran derivatives. Thus by boiling it with hydriodic acid it is reduced to 4 : *5-diphenyl*-2-tert.-*butylfurfuran* (m. p. 68—69·5°):

$$\begin{array}{l} C_6H_5\cdot C\!=\!CH \\ C_6H_5\cdot CO\ \ CO\cdot C(CH_3)_3 \end{array} + 2H = \begin{array}{c} C_6H_5\cdot C\!-\!CH \\ C_6H_5\cdot C\ \ \ C\cdot C(CH_3)_3 \\ \diagdown\ \diagup \\ O \end{array} + H_2O.$$

It interacts with hydrogen chloride in alcoholic solution to form 3-*chloro*-4 : 5-*diphenyl*-2-tert.-*butylfurfuran* (m. p. 87—88°):

$$\begin{array}{l} C_6H_5\cdot C\!=\!CH \\ C_6H_5\cdot CO\ \ CO\cdot C(CH_3)_3 \end{array} + HCl = \begin{array}{c} C_6H_5\cdot C\!-\!CCl \\ C_6H_5\cdot C\ \ \ C\cdot C(CH_3)_3 \\ \diagdown\ \diagup \\ O \end{array} + H_2O.$$

In like manner it interacts with acetic anhydride to which a few drops of concentrated sulphuric acid have been added, yielding 3-*acetoxy*-4 : 5-*diphenyl*-2-tert.-*butylfurfuran* (m. p. 99—100°). In this case the reaction consists in an addition of acetic acid to the unsaturated γ-diketone, followed by elimination of water:

$$\begin{array}{l} C_6H_5\cdot C\!=\!CH \\ C_6H_5\cdot CO\ \ CO\cdot C(CH_3)_3 \end{array} \longrightarrow \begin{array}{l} C_6H_5\cdot CH\cdot CH\cdot O\cdot C_2H_3O \\ C_6H_5\cdot CO\ \ CO\cdot C(CH_3)_3 \end{array} \longrightarrow \begin{array}{c} C_6H_5\cdot C\!-\!C\cdot O\cdot C_2H_3O \\ C_6H_5\cdot C\ \ \ C\cdot C(CH_3)_3 \\ \diagdown\ \diagup \\ O \end{array}$$

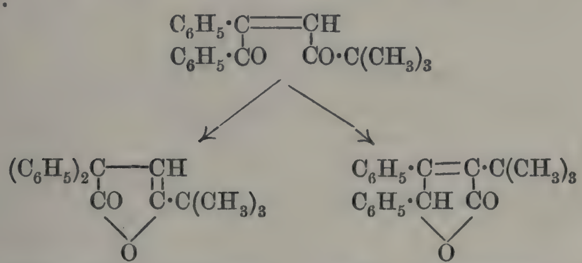
The corresponding reaction in the case of dibenzoylstyrene was discovered by J. Thiele (*Ber.*, 1898, 31, 1248). The mechanism of Thiele's reaction is the same as in the formation of chlorotriphenylfurfuran from dibenzoylstyrene and hydrogen chloride (Japp and Klingemann, *loc. cit.*, p. 663).

The two last-mentioned reactions cannot occur in the case of dibenzoylstilbene, as in this compound there is no hydrogen directly attached to the ethylene group.

Japp and Klingemann (*loc. cit.*, p. 665) showed that when dibenzoylstyrene is heated, it is for the most part converted into the isomeric triphenylcrotolactone (m. p. 117—118°):

a small quantity of the isomeric *trans*-dibenzoylstyrene being formed at the same time.

The action of heat on α-benzoyl-β-trimethacetylstyrene differs from the foregoing inasmuch as *two* isomeric crotolactones are formed, according as the necessary migration of a monad hydrocarbon radicle occurs in the benzil residue or in the methyl *tert.*-butyl ketone residue:



Crotolactone (m. p. 150°) derived from *αα-diphenyl-β-trimethacetylpropionic acid.*

Stable Δ^1-*crotolactone* (m. p. 75°) derived from *β-phenyl-α-*tert.-*butyl-β-benzoylpropionic acid.**

whilst no formation of the isomeric *trans* benzoyltrimethacetylstyrene was observed.

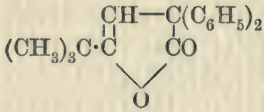
Dibenzoylstyrene might of course yield two isomeric crotolactones corresponding with the foregoing, according as the migration of a phenyl group occurred in the benzil residue or in the acetophenone residue; but only that formed according to the first of these processes was observed. Dibenzoylstilbene, on the other hand, with its symmetrical molecule, can yield only one crotolactone—tetraphenylcrotolactone, Zinin's so-called "tabular oxylepiden."

On oxidising the foregoing crotolactone melting at 150° with chromium trioxide, *benzophenone* was obtained, thus proving that a phenyl group had migrated in the formation of the crotolactone.

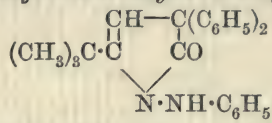
By the action of potassium hydroxide this crotolactone was

* The corresponding *labile* Δ^2-*crotolactone*, derived from the same ketonic acid, is described later on. The reasons for assigning respectively the Δ^1-unsaturated and Δ^2-unsaturated constitution to these crotolactones are to be found in J. Thiele's paper: "Ueber isomere Diphenylcrotonlactone" (*Annalen*, 1899, **306**, 194).

hydrolysed to *aa-diphenyl-β-trimethacetylpropionic acid* (m. p. 133—134°):

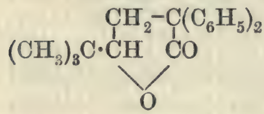
 $+ H_2O = C(CH_3)_3\cdot CO\cdot CH_2\cdot C(C_6H_5)_2\cdot CO_2H.$

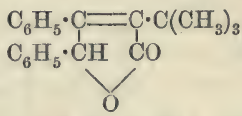
This acid interacts with phenylhydrazine, eliminating 2 mols. of water and yielding a compound, $C_{26}H_{26}ON_2$ (m. p. 143—145°) Following the analogy of the compound formed in the corresponding reaction of *aa*-diphenyl-*β*-benzoylpropionic acid with phenylhydrazine (Japp and Klingemann, *loc. cit.*, p. 665), this substance would be 1-*phenylamino-2-keto-3 : 3-diphenyl-5-*tert.*-butyl-2 : 3-dihydropyrrhole,*



When diphenyltrimethacetylpropionic acid is heated, or when it is allowed to remain at the ordinary temperature with acetic anhydride to which a few drops of concentrated sulphuric acid have been added, it is reconverted into the *crotolactone* melting at 150°.

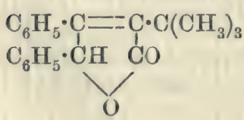
By treating diphenyltrimethacetylpropionic acid in boiling alcoholic solution with sodium, it is reduced to *aa-diphenyl-γ-*tert.*-butyl-γ-hydroxybutyric acid,* $C(CH_3)_3\cdot CH(OH)\cdot CH_2\cdot C(C_6H_5)_2\cdot CO_2H$, which, when liberated from the sodium salt, forms the *butyrolactone*,

 (m. p. 139—140°).

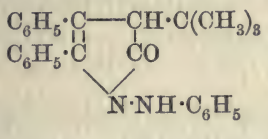
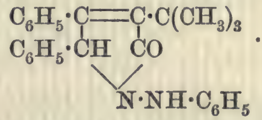
When the stable Δ^1-crotolactone,  (m. p. 75°),

is oxidised with chromium trioxide, it yields *benzil,* along with a crystalline product melting at 165—166°, the latter being obtained in quantity too small for identification. The formation of benzil shows that no migration of a phenyl group has occurred in the production of this lactone from benzoyltrimethacetylstyrene.

By the action of potassium hydroxide the Δ^1-crotolactone (m. p. 75°) is hydrolysed to *β-phenyl-a-*tert.*-butyl-β-benzoylpropionic acid* (m. p. 183—184°):

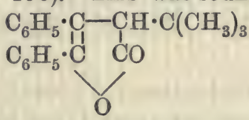
 $+ H_2O = C_6H_5\cdot CO\cdot CH(C_6H_5)\cdot CH(C(CH_3)_3)\cdot CO_2H$.

This acid (m. p. 183—184°) interacts with phenylhydrazine, eliminating 2 mols. of water and yielding a compound, $C_{26}H_{26}ON_2$ (m. p. 185—186°), which, on the analogy already referred to, might be either


or

.

By the action of heat, β-phenyl-α-*tert.*-butyl-β-benzoylpropionic acid is dehydrated, regenerating the foregoing stable Δ^1-*crotolactone* (m. p. 75°).

As this γ-ketonic acid has a hydrogen atom in the α-position, it ought to be convertible, by treatment at the ordinary temperature with acetic anhydride to which a few drops of concentrated sulphuric acid have been added, into a labile Δ^2-crotolactone (compare J. Thiele, *Annalen*, 1899, 306, 196). This was found to be the case, and the *labile Δ^2-crotolactone*,

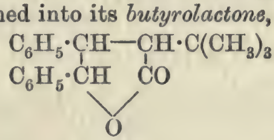


(m. p. 119°), was afterwards transformed, by boiling with acetic anhydride, into the *stable Δ^1-crotolactone* (m. p. 75°) already mentioned—a transformation described by Thiele in the case of other labile Δ^2-crotolactones.

β-Phenyl-α-*tert.*-butyl-β-benzoylpropionic acid, when treated in boiling alcoholic solution with metallic sodium, is reduced to *$\beta\gamma$-diphenyl-α-*tert.*-butyl-γ-hydroxybutyric acid,*

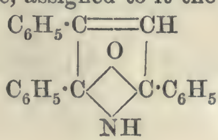
$$C_6H_5{\cdot}CH(OH){\cdot}CH(C_6H_5){\cdot}\underset{\displaystyle C(CH_3)_3}{\underset{|}{CH}}{\cdot}CO_2H\ ,$$

which, when liberated from the sodium salt, spontaneously eliminates water, and is transformed into its *butyrolactone*,

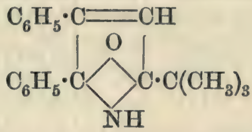


(m. p. 155·5°).

Benzoyltrimethacetylstyrene interacts with ammonia, eliminating water and yielding an *imide* (m. p. 152°) having the formula $C_{20}H_{21}ON$. Japp and Tingle, on the ground that the corresponding imide of dibenzoylstyrene yielded, on reduction, 2 : 4 : 5-triphenylpyrrhole and, by oxidation, dibenzamide, assigned to it the constitution

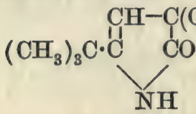

.

(Trans., 1897, **71**, 1140). If the analogy of this compound is to be followed, the present imide would have the constitution

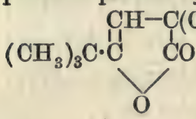


and might be termed 4 : 5-*diphenyl*-2-tert.-*butyl*-2 : 5-*oxidopyrrhole*.*

When this imide is heated above its melting point, it is converted into the isomeric 2-*keto*-3 : 3-*diphenyl*-5-tert.-*butyl*-2 : 3-*dihydropyrrhole*,

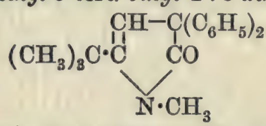


(m. p. 220°). The constitution of this compound is proved by its formation by the interaction of the crotolactone



(m. p. 150°) with ammonia.

By the action of methylamine on benzoyltrimethacetylstyrene, 2-*keto*-3 : 3-*diphenyl*-1-*methyl*-5-tert.-*butyl*-2 : 3-*dihydropyrrhole*,



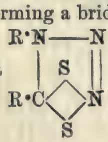
(m. p. 112°, not sharp), is produced. No intermediate compound corresponding with the imide is here formed.

Experimental.

I. *Preparation of* α-*Benzoyl*-β-*trimethacetylstyrene* (m. p. 115°).

Eighty grams of benzil, 48 grams of methyl *tert.*-butyl ketone, and 240 grams of absolute alcohol were warmed in a flask until the whole of the benzil had dissolved, after which the flask was rapidly cooled with water, shaking all the time so as to prevent the formation of large crystals of benzil. Sixteen grams of potassium hydroxide, dissolved in 24 grams of water, were then added, and the mixture was

* Regarding the use of the term "oxido" to indicate "bridge-oxygen," compare Japp and Michie (Trans., 1903, **83**, 281, footnote). M. Busch, on the other hand (*J. pr. Chem.*, 1903, [ii], **67**, 203), employs the prefix "endo" to denote a mobile atom forming a bridge between two atoms in a ring. Thus, compounds having the formula



are termed by him "*endo*thio-thiobiazolines."

left in the corked flask for a fortnight, shaking from time to time. The benzil gradually disappeared, whilst another crystalline substance was gradually deposited in its place. The crystalline deposit was separated by filtration, washed with water to remove a little potassium benzilate, and recrystallised twice from boiling alcohol. It was thus obtained in pointed prisms melting at 115°. By spontaneous evaporation of its alcoholic solution it is obtained in rhombs showing the same melting point. Analysis gave figures agreeing with the formula of *a-benzoyl-β-trimethacetylstyrene*,

$$\begin{array}{l} C_6H_5\cdot C\!=\!\!=\!\!=CH \\ C_6H_5\cdot CO \quad\;\; CO\cdot C(CH_3)_3 \end{array}.$$

0·1925 gave 0·5768 CO_2 and 0·1196 H_2O. C = 81·72; H = 6·90.
0·1498 „ 0·4496 CO_2 „ 0·0928 H_2O. C = 81·85; H = 6·89.
$C_{20}H_{20}O_2$ requires C = 82·19; H = 6·85 per cent.

The yield of once crystallised and practically pure substance was 71 grams, whilst more could be obtained from the mother liquor.

In extracting with alcohol the crude product which had previously been washed with water, a substance was obtained which was almost insoluble in alcohol. It was recrystallised from benzene, but different preparations gave discrepant melting points, varying between 160—163° and 177°, and did not give concordant figures on analysis. The quantity was too small for further examination.

An attempt to obtain a condensation compound of 1 mol. of benzil with 2 mols. of methyl *tert.*-butyl ketone, using an alcoholic solution of sodium ethoxide as a condensing agent, as in J. Wislicenus and A. Lehmann's method of preparing dibenzoyldiphenylbutadiene from benzil and acetophenone (*Annalen*, 1898, **302**, 198), yielded only impure benzoyltrimethacetylstyrene.

II. *Conversion of a-Benzoyl-β-trimethacetylstyrene into Furfuran Derivatives.*

Action of Hydriodic Acid on Benzoyltrimethacetylstyrene: Formation of 4:5-*Diphenyl*-2-tert.-*butylfurfuran*,

$$\begin{array}{l} C_6H_5\cdot C - CH \\ C_6H_5\cdot C \quad C\cdot C(CH_3)_3 \\ \qquad\quad\; O \end{array}$$

(m. p. 68—69·5°).—Three grams of finely-powdered benzoyltrimethacetylstyrene were boiled with fuming hydriodic acid (sp. gr. 1·96) for 5 minutes. The product was dissolved in ether, shaken successively with solutions of sulphurous acid and sodium carbonate, and the substance which remained after expelling the ether was distilled under

12 mm. pressure. The distillate, which passed over at 196—199°, weighed 2·3 grams; it was crystallised from methyl alcohol, from which it was deposited in four-sided, oblique plates, melting at 68—69·5°.

0·1616 gave 0·5125 CO_2 and 0·1044 H_2O. C = 86·49; H = 7·17.
0·1569 ,, 0·4987 CO_2 ,, 0·1023 H_2O. C = 86·68; H = 7·24.
$C_{20}H_{20}O$ requires C = 86·95; H = 7·24 per cent.

From dilute acetic acid the compound crystallises in aggregates of large, oblique laminæ, containing solvent of crystallisation.

*Action of Alcoholic Hydrogen Chloride on Benzoyltrimethacetylstyrene: Formation of 3-Chloro-4:5-diphenyl-2-*tert.*-butylfurfuran,*

$$\begin{array}{l} C_6H_5\cdot C\text{—}CCl \\ C_6H_5\cdot C \quad C\cdot C(CH_3)_3 \\ \quad\quad\diagdown\diagup \\ \quad\quad\; O \end{array}$$

(m. p. 87—88°).—Four grams of finely-powdered benzoyltrimethacetylstyrene were added to an excess of saturated alcoholic hydrogen chloride. The substance dissolved slowly in the cold, and the solution darkened slightly. In a few hours an oily product separated, which afterwards solidified. By recrystallisation from alcohol it was obtained in aggregates of long, slender, radiating needles, melting constantly at 87—88°.

0·4844 gave 0·2231 AgCl. Cl = 11·40.
$C_{20}H_{19}OCl$ requires Cl = 11·46 per cent.

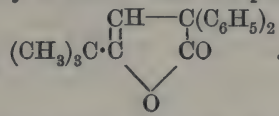
*Action of a Mixture of Acetic Anhydride and Sulphuric Acid on Benzoyltrimethacetylstyrene: Formation of 3-Acetoxy-4:5-diphenyl-2-*tert.*-butylfurfuran,*

$$\begin{array}{l} C_6H_5\cdot C\text{—}C\cdot O\cdot C_2H_3O \\ C_6H_5\cdot C \quad C\cdot C(CH_3)_3 \\ \quad\quad\diagdown\diagup \\ \quad\quad\; O \end{array}$$

(m. p. 99—100°).—Two grams of benzoyltrimethacetylstyrene were dissolved in the cold in 10 c.c. of acetic anhydride to which 4 drops of concentrated sulphuric acid had been added, and the mixture was left for a day. The solution, which became reddish-coloured on mixing, deposited a solid substance; this was separated by filtration and purified by recrystallisation from boiling alcohol. It was thus obtained in short, lustrous, white needles which turned yellow on exposure to light; they melted at 99—100°. The substance dissolves in concentrated sulphuric acid, giving a solution with a faint green fluorescence (compare *Ber.*, 1898, **31**, 1249).

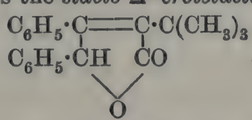
0·1677 gave 0·4850 CO_2 and 0·0998 H_2O. C = 78·87; H = 6·61.
$C_{22}H_{22}O_3$ requires C = 78·74; H = 6·59 per cent.

III. *Action of Heat on α-Benzoyl-β-trimethacetylstyrene.*

Ten grams of benzoyltrimethacetylstyrene were heated for half an hour in a test-tube jacketed with diphenylamine vapour (310°). Some gas was given off during the process, and the fused substance turned brown, whilst needles of a new compound melting at 150° condensed in the cooler parts of the tube. The resulting brown mass, dissolved in benzene, gave, on addition of light petroleum, slender needles melting constantly at 150°. This compound, as its reactions show, is the *crotolactone*,  .

0·1506 gave 0·4548 CO_2 and 0·0965 H_2O. C = 82·36 ; H = 7·11.
0·1595 „ 0·4803 CO_2 „ 0·1002 H_2O. C = 82·12 ; H = 6·98.
$C_{20}H_{20}O_2$ requires C = 82·19 ; H = 6·85 per cent.

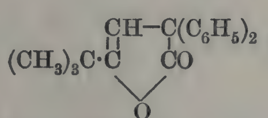
The mother liquor from the foregoing compound deposited thin plates, embedded in a yellow oil. By distilling this entire residue under reduced pressure, and recrystallising the distillate from alcohol, the substance was obtained in thin plates melting at 75°. Its reactions show that it is the *stable Δ^1-crotolactone*,

 .

0·1807 gave 0·5444 CO_2 and 0·1129 H_2O. C = 82·17 ; H = 6·94.
$C_{20}H_{20}O_2$ requires C = 82·19 ; H = 6·85 per cent.

In a preparation on a larger scale in which 71 grams of benzoyltrimethacetylstyrene were heated in four portions and the products worked up together the yields were: compound (m. p. 150°), 22 grams ; compound (m. p. 75°), 15 grams.

In one experiment a substance was obtained melting at about 212°, only sparingly soluble in the ordinary organic solvents although dissolving in solvent naphtha. The quantity was insufficient for further examination.

IV. *Crotolactone,*  (m. p. 150°), *derived from αα-Diphenyl-β-trimethacetylpropionic Acid,*

$C(CH_3)_3{\cdot}CO{\cdot}CH_2{\cdot}C(C_6H_5)_2{\cdot}CO_2H$ (m. p. 133—134°).

Oxidation of Crotolactone (m. p. 150°).—1·5 grams of the crotolactone (m. p. 150°) were dissolved in glacial acetic acid on the water bath, and an excess of chromium trioxide was gradually added, afterwards

continuing the heating for a quarter of an hour. Water was then added and the oil which separated was extracted with ether. The ethereal solution was shaken with a solution of sodium carbonate, after which the ether was expelled and the residue distilled under reduced pressure. The distillate, which passed over when the oil-bath was at 185° (12 mm. pressure) was slightly coloured; it smelt like benzophenone and solidified on touching it with a fragment of this substance. After spreading it on a porous tile to absorb oil, it melted at 46—48·5°. Mixed with a specimen of benzophenone (m. p. 48—49°) it melted at 48—49°. It was therefore *benzophenone.*

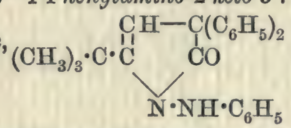
Action of Potassium Hydroxide on the Crotolactone (m. p. 150°): *Formation of αα-Diphenyl-β-trimethacetylpropionic Acid,* $C(CH_3)_3 \cdot CO \cdot CH_2 \cdot C(C_6H_5)_2 \cdot CO_2H$ (m. p. 133—134°). —A quantity of the crotolactone (m. p. 150°) was dissolved in alcoholic potassium hydroxide, and the mixture was evaporated to dryness on the water-bath. On dissolving the residue in water and acidifying, an oil was precipitated: this solidified to a hard mass. The substance, which was the ketonic acid sought for, was purified by recrystallisation from benzene with addition of light petroleum. It formed four-sided, oblique plates, with bevelled edges, and melted at 133—134°.

0·2038 gave 0·5774 CO_2 and 0·1336 H_2O. C = 77·27; H = 7·28.
$C_{20}H_{22}O_3$ requires C = 77·42; H = 7·10 per cent.

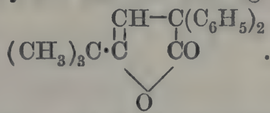
The *silver salt* was obtained as a white powder by precipitating a solution of the acid in ammonia with silver nitrate.

0·2416 gave 0·0640 Ag. Ag = 26·50.
$C_{20}H_{21}O_3Ag$ requires Ag = 25·90 per cent.

The crotolactone (m. p. 150°) was also transformed into the foregoing *αα-diphenyl-β-trimethacetylpropionic acid* (m. p. 133—134°) by boiling it for 4 minutes with fuming hydriodic acid (sp. gr. 1·9). An acid melting at 145—147° was formed at the same time, but the quantity was insufficient for further study.

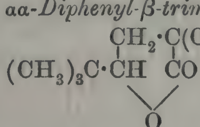
Action of Phenylhydrazine on αα-Diphenyl-β-trimethacetylpropionic Acid: Formation of 1-*Phenylamino*-2-*keto*-3 : 3-*diphenyl*-5-tert.-*butyl*-2 : 3-*dihydropyrrhole,*  (m. p. 143—145°).—Two grams of αα-diphenyl-β-trimethacetylpropionic acid (m. p. 133—134°) and 1·1 grams of phenylhydrazine, with a little absolute alcohol, were heated in a sealed tube at 150° for $1\frac{1}{2}$ hours. On allowing the tube to remain for 24 hours in the cold a crystalline substance was deposited; this was purified by recrystallisation from alcohol, from which it separated in leaflets melting at 143—145°.

0·1648 gave 0·4937 CO_2 and 0·1020 H_2O. C = 81·70 ; H = 6·88.
0·2278 ,, 14·90 c.c. moist nitrogen at 18° and 767 mm. N = 7·63.
$C_{26}H_{26}ON_2$ requires C = 81·67 ; H = 6·81 ; N = 7·33 per cent.

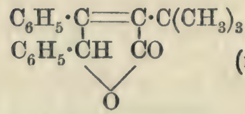
Action of Heat on $\alpha\alpha$-Diphenyl-β-trimethacetylpropionic Acid: Regeneration of the Crotolactone (m. p. 150°).—Half a gram of the acid was heated in a test-tube jacketed with diphenylamine vapour (310°), until bubbles (aqueous vapour) ceased to be given off. The product, which was somewhat dark-coloured, was purified by recrystallisation from benzene, with the addition of light petroleum. It was thus obtained in slender needles melting at 150°, which, by their physical properties and by the mixture melting-point test, were identified as the *crotolactone*,  .

Action of Acetic Anhydride containing a little Sulphuric Acid on $\alpha\alpha$-Diphenyl-β-trimethacetylpropionic Acid.—This reaction gave the same result as the foregoing. Eight c.c. of acetic anhydride were poured over 1 gram of $\alpha\alpha$-diphenyl-β-trimethacetylpropionic acid. On adding 1 drop of concentrated sulphuric acid, the organic acid immediately dissolved. On adding a second drop, a substance crystallised out. Water was added, and the precipitated substance was recrystallised from alcohol. By its physical properties and by the mixture melting-point test, it was identified as the foregoing *crotolactone* (m. p. 150°).

It should be noted that, in the case of the isomeric ketonic acid, to be described later on, two different crotolactones are obtained, according as the dehydration is effected by heating, or by the action of a mixture of acetic anhydride and sulphuric acid.

Reduction of $\alpha\alpha$-Diphenyl-β-trimethacetylpropionic Acid: Formation of the Lactone,  (m. p. 139—140°), *of $\alpha\alpha$-Diphenyl-γ-*tert.*-butyl-γ-hydroxybutyric Acid.*—2·8 grams of $\alpha\alpha$-diphenyl-β-trimethacetylpropionic acid (m. p. 133—134°) were dissolved in absolute alcohol, and 4 grams of sodium were gradually added to the boiling solution. The liquid was diluted with water and acidified, and the precipitated substance was purified by repeated crystallisation from alcohol. It formed slender needles melting at 139—140°. Analysis showed that the hydroxy-acid, formed by reduction, had parted with water, yielding the foregoing *butyrolactone*.

0·1574 gave 0·4713 CO_2 and 0·1054 H_2O. C = 81·66 ; H = 7·44.
$C_{20}H_{22}O_2$ requires C = 81·63 ; H = 7·48 per cent.

V. *Stable* Δ^1-*Crotolactone*,  (m. p. 75°), *derived from β-Phenyl-α-*tert.*-butyl-β-benzoylpropionic Acid*,

$$\begin{array}{l} C_6H_5\cdot CO\cdot CH(C_6H_5)\cdot CH\cdot CO_2H \\ \qquad\qquad\qquad\qquad\quad C(CH_3)_3 \end{array} \text{ (m. p. 183—184°).}$$

Oxidation of Crotolactone (m. p. 75°).—1·4 grams of the crotolactone were dissolved in glacial acetic acid on the water-bath and to the hot solution an excess of chromium trioxide was gradually added. The solution was diluted with water and extracted with ether. The ethereal extract was shaken with a solution of carbonate. On expelling the ether a gummy mass remained, which speedily became crystalline; this was separated by fractional crystallisation from light petroleum into two substances: long, yellow needles of *benzil* (m. p. 95°) further identified by the mixture melting-point test; and small, colourless crystals of a compound melting at 165—166°, the quantity of which was insufficient for further investigation.

Action of Potassium Hydroxide on the Crotolactone (m. p. 75°): *Formation of β-Phenyl-α-*tert.*-butyl-β-benzoylpropionic Acid*,

$$\begin{array}{l} C_6H_5\cdot CO\cdot CH(C_6H_5)\cdot CH\cdot CO_2H \\ \qquad\qquad\qquad\qquad\quad C(CH_3)_3 \end{array}$$

(m. p. 183—184°).—A quantity of the crotolactone (m. p. 75°) was heated on the water-bath with alcoholic potassium hydroxide until the alcohol was almost entirely expelled. The product dissolved completely in water, and, on acidifying, an organic acid was precipitated. This substance required repeated crystallisation from alcohol before it could be obtained pure. It crystallises in small prisms or slender needles, melting at 183—184°. Analysis showed that it had the expected composition.

0·1446 gave 0·4086 CO_2 and 0·0922 H_2O. C = 77·07; H = 7·08.
$C_{20}H_{22}O_3$ requires C = 77·42; H = 7·10 per cent.

The alcoholic mother liquor from the foregoing acid deposited a substance melting at 194—195°, the quantity of which was too small for further investigation.

The *silver salt* of β-phenyl-α-*tert.*-butyl-β-benzoylpropionic acid was obtained as a white precipitate by adding silver nitrate to a solution of the ammonium salt.

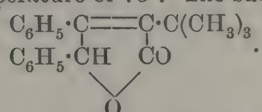
0·4354 gave 0·1100 Ag. Ag = 25·26.
$C_{20}H_{21}O_3Ag$ requires Ag = 25·90 per cent.

*Action of Phenylhydrazine on β-Phenyl-α-*tert.*-butyl-β-benzoylpropionic Acid.*—1·5 grams of the acid and 1 gram of phenylhydrazine were heated in alcoholic solution in a sealed tube for 2½ hours at 160°. The crystallisation of the product had to be started by rubbing the sides of the tube with a glass rod. The compound crystallised from alcohol in short prisms melting at 185—186°.

0·1598 gave 0·4756 CO_2 and 0·0983 H_2O. C = 81·17 ; H = 6·83.
0·2014 ,, 13·00 c.c. moist nitrogen at 15·5° and 756 mm. N = 7·51.
$C_{26}H_{26}ON_2$ requires C = 81·67 ; H = 6·81 ; N = 7·33 per cent.

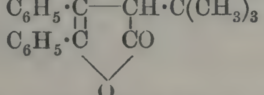
The question of the constitution of this compound is discussed in the introduction to the present paper.

*Dehydration of β-Phenyl-α-*tert.*-butyl-β-benzoylpropionic Acid: Regeneration of the Stable Δ¹-Crotolactone* (m. p. 75°).—A small quantity of the acid (m. p. 183—184°) was heated in diphenylamine vapour (310°) as described in the case of the corresponding experiment with the isomeric ketonic acid, continuing the heating until bubbles of aqueous vapour ceased to be given off. The product, which was slightly coloured, was purified by recrystallisation from alcohol. The quantity was insufficient for complete purification, so that the melting point was found at 71—72°, instead of 75°. A mixture of the substance with a specimen of the pure crotolactone (m. p. 75°) melted at the intermediate temperature of 73°. The substance was therefore the *stable Δ¹-crotolactone,*



By boiling the acid (m. p. 183—184°) for 4 minutes with fuming hydriodic acid (sp. gr. 1·9) the same dehydration occurred, and the *stable Δ¹-crotolactone* (m. p. 75°) was obtained. This result was confirmed by the mixture melting-point test. This reaction is precisely the reverse of that which occurs in the case of the crotolactone (m. p. 150°), as the latter compound is, as already described, hydrolysed by hydriodic acid to the corresponding ketonic acid (m. p. 133—134°).

*Action of Acetic Anhydride containing a little Sulphuric Acid on β-Phenyl-α-*tert.*-butyl-β-benzoylpropionic Acid: Formation of the Labile Δ²-Crotolactone,*



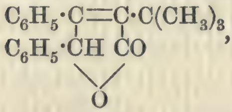
(m. p. 119°).—Ten c.c. of acetic anhydride were poured over 1·3 grams of the acid (m. p. 183—184°), and 4 drops of concentrated sulphuric acid were added. After some time, the solution was poured into water. The white solid which was precipitated was recrystallised twice from alcohol; it was thus obtained in long, slender needles, melting at 119°

0·1692 gave 0·5112 CO_2 and 0·1053 H_2O. C = 82·40 ; H = 6·91.
$C_{20}H_{20}O_2$ requires C = 82·19 ; H = 6·85 per cent.

The yield was 1·1 grams of once recrystallised substance.

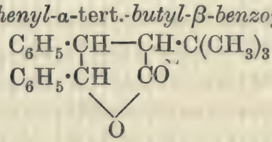
A small quantity of this labile Δ^2-crotolactone (m. p. 119°) was heated with alcoholic sodium hydroxide on the water-bath. On diluting with water and acidifying, *β-phenyl-α-*tert.*-butyl-β-benzoylpropionic acid* was precipitated. It was identified by the mixture melting-point test.

A further quantity of the labile Δ^2-crotolactone was boiled with acetic anhydride for 2½ hours. The product, precipitated with water and recrystallised from light petroleum, melted at 75—76° and was identified by the mixture melting-point test as the *stable* Δ^1*-crotolactone*,



, into which the labile compound had thus been converted (compare J. Thiele, *Annalen*, 1899, 306, 196).

*Reduction of β-Phenyl-α-*tert.*-butyl-β-benzoylpropionic Acid : Formation of the Lactone,*



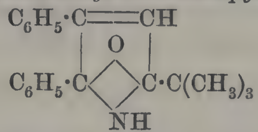
(m. p. 155·5°), *of βγ-Diphenyl-α-*tert.*-butyl-γ-hydroxybutyric Acid.*—Six grams of the acid (m. p. 183—184°) were dissolved in absolute alcohol, and 8 grams of sodium were gradually added to the boiling solution, which assumed a reddish colour. On adding water a turbidity was produced ; this was removed by filtration, and, on acidifying the filtrate, a pasty mass was precipitated which afterwards became hard. The substance was purified by recrystallisation both from alcohol and from light petroleum. From the latter solvent it was deposited in small needles melting at 155·5°. Analysis showed that the hydroxy-acid, formed by reduction of the ketonic acid, had parted with water, yielding the foregoing *butyrolactone.*

0·1685 gave 0·5022 CO_2 and 0·1143 H_2O. C = 81·28 ; H = 7·54.
$C_{20}H_{22}O_2$ requires C = 81·63 ; H = 7·48 per cent.

The first alcoholic mother liquor gave crystals of unaltered acid (m. p. 183—184°) which were removed by extracting with sodium carbonate solution.

VI. *Action of Ammonia and Methylamine on α-Benzoyl-β-trimethacetylstyrene.*

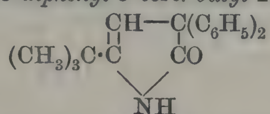
Action of Ammonia on α-Benzoyl-β-trimethacetylstyrene: Formation of 4 : 5-*Diphenyl*-2-tert.-*butyl*-2 : 5-*oxidopyrrhole*,



(m.p. 152°).—To a hot saturated, alcoholic solution of 5 grams of benzoyltrimethacetylstyrene an equal bulk of saturated alcoholic ammonia was added. As the liquid cooled, crystals were deposited. These were filtered off after 24 hours; the filtrate, diluted with water, gave a further crystalline precipitate. By recrystallisation from alcohol the substance was obtained in large, clear, six-sided prisms melting at 152°, and resolidifying even if kept somewhat above that temperature. The yield was about 4 grams.

0·1528 gave 0·4610 CO_2 and 0·1009 H_2O. C = 82·30; H = 7·33.
0·2594 „ 10·4 c.c. moist nitrogen at 7·5° and 775 mm. N = 4·94.
$C_{20}H_{21}ON$ requires C = 82·47; H = 7·22; N = 4·81 per cent.

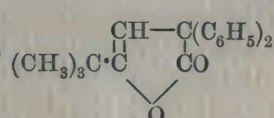
Action of Heat on 4 : 5-*Diphenyl*-2-tert.-*butyl*-2 : 5-*oxidopyrrhole*: *Formation of* 2-*Keto*-3 : 3-*diphenyl*-5-tert.-*butyl*-2 : 3-*dihydropyrrhole*,



(m. p. 220°).—Two grams of the foregoing oxidopyrrhole (m. p. 152°) were melted in a paraffin bath and kept at a temperature a little above the melting point. At this temperature the substance speedily resolidified; the product, which was reddish coloured, was boiled with a little alcohol to remove the colouring matter, and the residue was recrystallised from boiling alcohol. It formed long needles, or flat, obliquely truncated prisms melting at 220°.

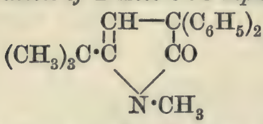
0·1656 gave 0·4978 CO_2 and 0·1114 H_2O. C = 81·98; H = 7·47.
0·3044 „ 13·1 c.c. moist nitrogen at 9° and 754 mm. N = 5·10.
$C_{20}H_{21}ON$ requires C = 82·47; H = 7·22; N = 4·81 per cent.

The constitution of the foregoing compound is proved by the following synthesis:

Half a gram of the crotolactone,  (m. p.

150°), was heated with strong alcoholic ammonia in a sealed tube at 130° for 3 hours. On cooling, the solution deposited small prisms melting at 219—220°, which proved to be 2-*keto*-3 : 3-*diphenyl*-5-tert.-*butyl*-2 : 3-*dihydropyrrhole*. The substance was further identified by the mixture melting-point test.

Action of Methylamine on α-Benzoyl-β-trimethacetylstyrene : Formation of 2-*Keto*-3 : 3-*diphenyl*-1-*methyl*-5-tert.-*butyl*-2 : 3-*dihydropyrrhole*,



(m. p. 112°, not sharp).—To a hot saturated solution of 4 grams of benzoyltrimethacetylstyrene in absolute alcohol an equal bulk of a 20 per cent. solution of methylamine in alcohol was added. In a few hours crystals separated. Purified by recrystallisation from alcohol they formed stout, eight-sided prisms melting at 112° (not sharp).

0·1546 gave 0·4672 CO_2 and 0·1050 H_2O. C = 82·41 ; H = 7·54.
0·2666 ,, 10·9 c.c. moist nitrogen at 17° and 744 mm. N = 4·64.
$C_{21}H_{23}ON$ requires C = 82·62 ; H = 7·54 ; N = 4·59 per cent.

A quantity of the substance, heated in a paraffin bath at 150° for 15 minutes, was recovered unchanged.

We have to thank the Council of the Royal Society for an allotment from the Government Grant in aid of the work described in this and the two preceding papers.

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Some Derivatives of Anhydracetonebenzil.

By FRANCIS ROBERT JAPP, F.R.S., and JOSEPH KNOX, B.Sc., Carnegie Scholar in the University of Aberdeen.

THE condensations of benzil with saturated aliphatic ketones to form anhydracetonebenzil and its homologues have been studied in considerable detail by one of us in conjunction with various collaborators. It appeared of interest to ascertain what course the reaction would take in the case of an unsaturated ketone and to compare the product with that obtained from the corresponding saturated ketone. We selected for this purpose, as an unsaturated ketone, methyl *iso*butenyl ketone, $CH_3 \cdot CO \cdot CH \colon C(CH_3)_2$, and, as a saturated ketone, methyl *iso*butyl ketone.

Methyl *iso*butenyl ketone condenses with benzil under the influence of potassium hydroxide to form *β*-iso*propylideneanhydracetonebenzil*,

$$\begin{array}{l} C_6H_5 \cdot C{=\!=\!=}CH \diagdown \\ \quad\;\; | \qquad\qquad\quad >CO \\ C_6H_5 \cdot C(OH) \cdot C{=}C(CH_3)_2 \diagup \end{array}$$

(m. p. 205·5°), the reaction thus taking place exactly as in the case of the saturated ketones already studied, except that the presence of the bivalent *iso*propylidene group prevents the simultaneous formation of an isomeric *a*-compound. This condensation compound yields an *acetyl* derivative (m. p. 139—140° and 154—155°, dimorphous), the formation of which is rendered possible by the circumstance that the condensation compound has no hydrogen in the *β*-position, as otherwise derivatives of anhydracetonebenzil merely undergo dehydration under the influence of acetic anhydride. When reduced by brief boiling with hydriodic acid, *β*-*iso*propylideneanhydracetonebenzil yields *diphenyl*iso*propylidene*cyclo*pentenone*,

$$\begin{array}{l} C_6H_5 \cdot C \cdot CH_2 \diagdown \\ \qquad\;\; \| \qquad\quad >CO \\ C_6H_5 \cdot C{-\!-\!-}C{=}C(CH_3)_2 \diagup \end{array}$$

(m. p. 171°), the usual change in the position of the double bonds, so as to form a stilbene group, occurring during the process (compare Japp and Murray, Trans., 1897, **71**, 145; Japp and Meldrum, 1901, **79**, 1026).

Methyl *iso*butyl ketone and benzil, when condensed by means of potassium hydroxide, yield a mixture of *a*-iso*propylanhydracetonebenzil*,

$$\begin{array}{l} C_6H_5\cdot C\!=\!\!=\!\!=\!C\!-\!CH(CH_3)_2 \\ \qquad\qquad\qquad\quad >CO \\ C_6H_5\cdot C(OH)\cdot CH_2 \end{array}$$ (m. p. 142°), and *β*-iso*propylanhydr-acetonebenzil*,

$$\begin{array}{l} C_6H_5\cdot C\!=\!\!=\!CH \\ \quad | \qquad\qquad\quad >CO \\ C_6H_5\cdot C(OH)\cdot CH\!-\!CH(CH_3)_2 \end{array}$$ (m. p. 161·5°). The

former compound condenses with benzaldehyde, under the influence of potassium hydroxide, to yield *benzylidene-α-*iso*propylanhydracetone-benzil*,

$$\begin{array}{l} C_6H_5\cdot C\!=\!\!=\!\!=\!C\!-\!CH(CH_3)_2 \\ \quad | \qquad\qquad\quad >CO \\ C_6H_5\cdot C(OH)\cdot C\!=\!CH\cdot C_6H_5 \end{array}$$ (m. p. 179°).

We had originally contemplated carrying out the complete reduction of *β-iso*propylideneanhydracetonebenzil, and of one of the *iso*propyl-anhydracetonebenzils, with hydriodic acid and red phosphorus, so as to obtain, if possible, from both compounds the same hydrocarbon—diphenyl*iso*propyl*cyclo*pentane—and thus to prove more conclusively the relation existing between them; but the separation of the two *iso*propylanhydracetonebenzils was so difficult that we were compelled to relinquish our intention. Moreover, a preliminary experiment showed that the reduction of *β-iso*propylideneacetonebenzil beyond the *cyclo*pentenone stage did not yield a very satisfactory product.

At the end of the present paper we describe improved methods for the preparation of anhydracetonebenzil and *β*-methylanhydracetone-benzil.

Experimental.

I. *Condensation of Benzil with Methyl* iso*Butenyl Ketone.*

β-iso*Propylideneanhydracetonebenzil*, $$\begin{array}{l} C_6H_5\cdot C\!=\!CH \\ \quad | \qquad\qquad\quad >CO \\ C_6H_5\cdot C(OH)\cdot C\!=\!C(CH_3)_2 \end{array}$$.—

Twenty grams of benzil, 15 grams of methyl *iso*butenyl ketone ("mesityl oxide"), and 15 c.c. of an aqueous solution of potassium hydroxide of 33·3 per cent. strength were introduced into a conical flask fitted with a condensing tube, and the whole was heated for 4 hours on a thin metal plate over a water-bath,* the flask being shaken from time to time. The product, which was very dark-coloured, was poured into warm water, when a black, oily substance separated; this was washed with water and then left until it became semi-solid, after which it was spread on a porous tile. The substance, freed from adhering oil, was recrystallised several times from hot benzene and was thus obtained in slender, yellow needles melting at 205·5°. The yield was 7 grams.

* This arrangement gives a temperature of from 60° to 70°, provided that no steam is allowed to condense between the plate and the flask.

0·1632 gave 0·4929 CO_2 and 0·0911 H_2O. C = 82·37 ; H = 6·20.

$C_{20}H_{18}O_2$ requires C = 82·76 ; H = 6·20 per cent.

The same substance was obtained by condensing benzil with methyl *iso*butenyl ketone in the cold by means of a 0·5 per cent. solution of potassium hydroxide in absolute alcohol ; but the yield was even poorer than in the preceding case.

A portion of the substance was heated for 10 minutes at 310° (diphenylamine vapour) in an atmosphere of carbon dioxide. It resolidified on cooling and, after recrystallisation from benzene, was found to consist of unchanged substance (m. p. 205·5°). A sublimate which had formed in the upper part of the tube gave the same melting point.

The foregoing result shows that the condensation product is a closed-chain compound, inasmuch as all open-chain compounds formed by the condensation of benzil with ketones are changed on heating, yielding closed-chain compounds. Thus desylene-methyl ethyl ketone is in this way transformed into β-methylanhydracetonebenzil (Japp and Meldrum, Trans., 1901, **79**, 1031).

An attempt to synthesise β-*iso*propylideneanhydracetonebenzil by condensing acetone with anhydracetonebenzil under the influence of alcoholic potassium hydroxide—a process which, if benzaldehyde be substituted for acetone, readily yields benzylideneanhydracetonebenzil —led to no result.

Acetyl Derivative.—One gram of β-*iso*propylideneanhydracetonebenzil and 10 grams of acetic anhydride were mixed, and 1 drop of concentrated sulphuric acid was added. (If this proportion of acid is exceeded, a very impure product is obtained.) This addition caused the solid substance to dissolve, yielding a dark brown solution. After three days the mixture was poured into excess of water, and the yellow, flocculent precipitate which gradually separated, was purified by recrystallisation, first from alcohol, afterwards from benzene with addition of light petroleum (sp. gr. 0·71—0·72), and finally from light petroleum alone. It was thus obtained in slender, colourless needles. It melts at 139—140° and, if kept a little above this temperature, resolidifies, finally melting at 154—155°. This phenomenon is doubtless due to dimorphism, and not to chemical change, inasmuch as a specimen which had been melted as above, then allowed to cool, and recrystallised from light petroleum, again gave the same two melting points.

Analysis showed that a *monacetyl* derivative had been formed.

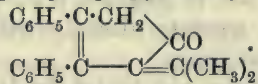
0·1566 gave 0·4570 CO_2 and 0·0857 H_2O. C = 79·58 ; H = 6·08.

$C_{22}H_{20}O_3$ requires C = 79·51 ; H = 6·02 per cent.

β-*iso*Propylideneanhydracetonebenzil is not acetylated by boiling it

for 4 hours with a mixture of acetic anhydride and anhydrous sodium acetate.

*Reduction of β-*iso*Propylideneanhydracetonebenzil with Hydriodic Acid: Formation of Diphenyl*iso*propylidene*cyclo*pentenone,*

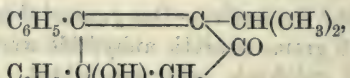


—Two grams of β-*iso*propylideneanhydracetonebenzil (m. p. 205·5°) were boiled for 8 minutes with 40 grams of fuming hydriodic acid (sp. gr. 1·96). Water was added, the organic substance was dissolved in ether, and the ethereal solution was shaken successively with aqueous sulphurous acid, sodium carbonate solution, and water. During the latter part of the process, a crystalline substance separated from the ether; it was filtered off and recrystallised from benzene, from which it was deposited in thick prisms melting constantly at 171°. The dried ethereal filtrate, on evaporation, yielded a further quantity of this substance, which was purified in the same way. Yield: 0·6 gram.

0·1448 gave 0·4647 CO_2 and 0·0863 H_2O. C = 87·52; H = 6·62.
$C_{20}H_{18}O$ requires C = 87·59; H = 6·57 per cent.

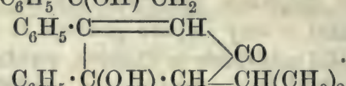
II. *Condensation of Benzil with Methyl* iso*Butyl Ketone.*

α-iso*Propylanhydracetonebenzil,*



and

β-iso*Propylanhydracetonebenzil,*



—Forty grams of finely powdered benzil, 28 grams of methyl *iso*butyl ketone, and 400 c.c. of a 0·5 per cent. solution of potassium hydroxide in absolute alcohol were shaken in a corked flask until the benzil had dissolved, after which the mixture was left for 12 days. The solution was then diluted with water until it became turbid, and allowed to crystallise. The crystalline deposit, which weighed 51 grams, proved to be a mixture of two substances—one of them dimorphous—which were very difficult to separate. Fractional crystallisation proved unavailing, although nearly all the ordinary organic solvents were tried. Finally we had to resort to the tedious process of picking out the different kinds of crystals. The crystalline product was dissolved in benzene, and somewhat less than an equal volume of light petroleum (sp. gr. 0·71—0·72) was added. The solution deposited colourless, six-sided prisms, white, silky needles, and flat, yellow prisms. The three kinds of crystals were separated mechanically.

The six-sided prisms were recrystallised repeatedly from benzene with the addition of light petroleum until they showed the constant melting point of 142°. The white, silky needles also melted at 142°, and a mixture of these with the six-sided prisms gave no depression of melting point. When either the six-sided prisms or the silky needles are crystallised from benzene with addition of light petroleum, a mixture of prisms and needles is obtained in each case. When a mixture of the prisms and needles is allowed to stand with a mixture of benzene and light petroleum insufficient to dissolve them, the needles gradually disappear, being transformed into the prisms. The substance melting at 142° is thus dimorphous, the six-sided prisms being the stable form at the ordinary temperature. This substance is α-iso*propylanhydracetonebenzil*, as is shown by its yielding a benzylidene derivative (*v. infra*).

0·2151 gave 0·6477 CO_2 and 0·1339 H_2O. C = 82·12 ; H = 6·91.
$C_{20}H_{20}O_2$ requires C = 82·19 ; H = 6·84 per cent.

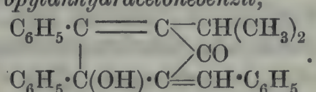
This compound (m. p. 142°) was recovered unchanged after being heated for 5 minutes at 330° in an atmosphere of carbon dioxide. This result indicates that the substance is a closed-chain condensation product, as formulated.

The flat, yellow prisms were recrystallised from light petroleum (sp. gr. 0·71—0·72). The compound, which is β-iso*propylanhydracetonebenzil*, was thus obtained in flat, colourless needles, melting constantly at 161·5°. β-Monalkylanhydracetonebenzils melt higher than the corresponding α-derivatives.

0·1563 gave 0·4711 CO_2 and 0·0980 H_2O. C = 82·20 ; H = 6·96.
$C_{20}H_{20}O_2$ requires C = 82·19 ; H = 6·84 per cent.

The quantity of this compound was too small, and its separation too difficult, to allow of our investigating it further.

*Benzylidene-α-*iso*propylanhydracetonebenzil*,



—One gram of α-*iso*propylanhydracetonebenzil (m. p. 142°) and 0·4 gram of benzaldehyde were shaken with a 1 per cent. solution of potassium hydroxide in absolute alcohol until the whole dissolved. After 12 days the liquid was diluted with half its volume of water. The crystals which were deposited weighed 1 gram. They were twice recrystallised from benzene, with the addition of light petroleum, and were thus obtained in the form of four-sided prisms, with oblique or pointed ends. They melted constantly at 179°.

0·1623 gave 0·5062 CO_2 and 0·0948 H_2O. C = 85·06 ; H = 6·49.
$C_{27}H_{24}O_2$ requires C = 85·26 ; H = 6·31 per cent.

III. *Improved Methods of Preparing Anhydracetonebenzil and β-Methylanhydracetonebenzil.*

Anhydracetonebenzil.—Acetonebenzil, $\begin{array}{l} C_6H_5\cdot CO \\ \quad | \\ C_6H_5\cdot C(OH)\cdot CH_2\cdot CO\cdot CH_3 \end{array}$, and anhydracetonebenzil, $\left.\begin{array}{l} C_6H_5\cdot C{=\!=\!=}CH \\ \quad | \\ C_6H_5\cdot C(OH)\cdot CH_2 \end{array}\right>CO$, were first prepared by Japp and Miller (Trans., 1885, 47, 21 and 27), who, however, assigned to the latter compound a constitution different from the foregoing and termed it "dehydracetonebenzil." The former compound was obtained by the action of a small quantity of aqueous potassium hydroxide on a mixture of benzil and acetone, the latter was formed from the same substances when an excess of potassium hydroxide was used.

Both of these substances were subsequently prepared on several occasions; but the yields varied in an unaccountable manner. It was evident that much depended on the character of the acetone. Japp and Miller found that a specimen of acetone purified merely by fractional distillation could not be used in the preparation of acetonebenzil. They say: "The employment of an acetone purified by means of the bisulphite compound is in this reaction *indispensable*—not merely for obtaining a good yield of the compound, but in order to obtain any of the compound at all." Japp and Klingemann, however (Trans., 1890, 57, 673, footnote), found that acetone could be prepared so pure as not to give the reaction, but that the same acetone readily condensed with benzil under the influence of a little aqueous potassium hydroxide to form acetonebenzil, if two or three drops of alcohol were previously added to it.*

We have now had a similar experience in the preparation of anhydracetonebenzil. Working according to the directions given by Japp and Lander (Trans., 1897, 71, 130), who improved upon the original process, and using Kahlbaum's "acetone from the bisulphite compound," we obtained hardly any anhydracetonebenzil, the greater part of the benzil being recovered unchanged. This was the more surprising, as Japp and Lander, in preparing the very large quantities of anhydracetonebenzil which they required for their study of the oxidation of this compound, had not merely employed this method, but had used acetone of the same quality, also obtained from Kahlbaum, although of a different preparation.

Mindful of Japp and Klingemann's experience with acetonebenzil, we repeated the process, adding, however, a few drops of alcohol to the

* I pointed out (*loc. cit.*) that the "pure" acetone prepared by Dr. Miller and myself may have contained traces of alcohol derived from the commercial ether which was used in washing the bisulphite compound.—F. R. J.

mixture. The effect was such that we obtained a yield even better than that recorded by Japp and Lander.

As this slight modification may thus mean all the difference between failure and success in the preparation of anhydracetonebenzil, and as it renders the course of the reaction independent of minute differences in the quality of the acetone employed, we will describe the method in detail.

Two hundred grams of finely-powdered benzil, 125 grams of pure acetone (Kahlbaum's acetone "from the bisulphite compound"), 1 c.c. of alcohol, and 2 c.c. of an aqueous solution of potassium hydroxide of 33·3 per cent. strength were shaken in a corked flask until the whole of the benzil had dissolved. The liquid became slightly warm during the process, owing to the formation of the aldol condensation compound, acetonebenzil. Fifty more c.c. of the aqueous potassium hydroxide were then added, and the mixture was warmed for half an hour on the water-bath, during which time it was frequently shaken. The whole was then poured into hot water, and the organic substance, which solidified on cooling, was ground in a mortar, washed, first with hot water and then with a little ether to remove dark-coloured impurities, and finally recrystallised from hot benzene. In this way we obtained, from the foregoing quantities, 165 grams of anhydracetonebenzil (m. p. 147° *), without working up the mother liquors, whereas Japp and Lander, who did not add alcohol to the mixture, obtained only 150 grams in all.

It must be borne in mind that although the addition of a small quantity of alcohol thus facilitates the occurrence of the reaction, the condensation of benzil and acetone to form anhydracetonebenzil cannot be effected by means of an alcoholic solution of potassium hydroxide, since under these circumstances the anhydracetonebenzil formed in the first instance condenses with a second molecule of benzil to form anhydracetonedibenzil.

β-Methylanhydracetonebenzil.—Of the two monomethyl homologues of anhydracetonebenzil—α-methylanhydracetonebenzil,

$$\begin{matrix} C_6H_5\cdot C = C(CH_3) \\ C_6H_5\cdot C(OH)\cdot CH_2 \end{matrix} > CO,$$

and β-methylanhydracetonebenzil, $\begin{matrix} C_6H_5\cdot C = \!=\!=\!=\!= CH \\ C_6H_5\cdot C(OH)\cdot CH(CH_3) \end{matrix} > CO$ — the α-compound is readily obtained, together with only a mere trace of the

* This is the melting point of *yellow* anhydracetonebenzil as ordinarily obtained, the yellow colour being due to the presence of a trace of benzylideneanhydracetonebenzil which cannot be removed except by a wasteful process of partial oxidation of the substance. The pure compound is colourless and melts at 149°, but the yellow substance is sufficiently pure for all ordinary purposes (compare Japp and Miller, Trans., 1885, **47**, 27; Japp and Findlay, 1899, **75**, 1018 and 1019).

β-compound, by the protracted action of a 0·5 per cent. solution of potassium hydroxide in absolute alcohol on a mixture of benzil and methyl ethyl ketone in the cold; whereas, when *aqueous* potassium hydroxide of 33·3 per cent. strength is used, and the mixture is heated, the proportion of β-compound formed is increased, remaining, however, below that of the α-compound which is simultaneously produced, so that the yield of β-compound still leaves much to be desired (Japp and Meldrum, Trans., 1901, **79**, 1028).

We now find that by substituting aqueous sodium hydroxide for potassium hydroxide in the latter reaction the yield of β-compound is very appreciably improved.

Eighty grams of benzil, 50 grams of methyl ethyl ketone, 0·5 c.c. of alcohol, and 60 c.c. of a solution of sodium hydroxide prepared by dissolving the *commercial* * hydroxide in twice its weight of water, were introduced into a conical flask fitted with a condensing tube, and the whole was heated for 3½ hours on a thin metal plate over a water-bath, the flask being shaken from time to time. The product was poured into hot water, and the solidified substance was ground, washed with water, freed from dark-coloured impurities by treatment with a little ether, and dissolved in boiling alcohol. The solution, on cooling, deposited 24 grams of practically pure β-methylanhydracetonebenzil. The mother liquor contained α-methylanhydracetonebenzil and α-desylenemethyl ethyl ketone, together with a small quantity of β-methylanhydracetonebenzil; these could be separated by fractional crystallisation from alcohol. It is to be noted that desylenemethyl ethyl ketone can be converted quantitatively into β-methylanhydracetonebenzil by heating it for a short time at 330° (Japp and Meldrum, Trans., 1901, **79**, 1031).

A second experiment conducted in the same way also gave 24 grams of the β-compound, whereas in a previous experiment in which the same quantities of benzil and methyl ethyl ketone were heated with aqueous *potassium* hydroxide of 33·3 per cent. strength only 19 grams were obtained.

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* In one experiment, in which we employed *pure* sodium hydroxide, the solution made up in the above proportions proved to be too strong, and considerable resinification of the organic substances occurred.

*The Dihydrocyanides of Benzil and Phenanthraquinone.**

By Francis Robert Japp, F.R.S., and Joseph Knox, B.Sc., Carnegie Scholar in the University of Aberdeen.

Although the dihydrocyanides of α-diketones are most generally formulated as tartronitriles, no strict proof that they possess this constitution has hitherto been given, with the exception of the hydrolysis of Zinin's benzildihydrocyanide, $\begin{array}{l} C_6H_5\cdot C(OH)\cdot CN \\ C_6H_5\cdot C(OH)\cdot CN \end{array}$, to diphenyltartramide (Burton, *Ber.*, 1883, **16**, 2232). Indeed, owing to the ease with which these compounds break up into α-diketone and hydrocyanic acid, some writers have preferred to represent them as molecular combinations.

We have obtained conclusive evidence of the tartronitrile constitution of these compounds by preparing their *diacetyl* derivatives. The dihydrocyanides which we have studied in this direction are: (1) benzildihydrocyanide; (2) the phenanthraquinonedihydrocyanide obtained by Japp and Miller; and (3) a stereoisomeric phenanthraquinonedihydrocyanide described in the present paper.

By treatment with concentrated sulphuric acid in the cold, benzildihydrocyanide is converted into *diphenylacetamide*. In order to account for this reaction it is necessary to assume that, as a first stage, a pinacoline migration occurs:

$$\begin{array}{l} C_6H_5\cdot C(OH)\cdot CN \\ C_6H_5\cdot C(OH)\cdot CN \end{array} \longrightarrow \begin{array}{l} (C_6H_5)_2C\cdot CN \\ \qquad C(OH)_2\cdot CN \end{array},$$

the resulting compound then undergoing hydrolytic fission with formation of diphenylacetamide, $(C_6H_5)_2CH\cdot CONH_2$, and possibly oxalic acid.

By the interaction of phenanthraquinone with 30 per cent. aqueous hydrocyanic acid in the cold, Japp and Miller (Trans., 1887, **51**, 32) obtained a phenanthraquinonedihydrocyanide crystallising in slender needles. We find that a stronger solution of hydrocyanic acid is practically without action on phenanthraquinone in the cold, but that, on heating the mixture at 50°, a *stereoisomeric phenanthraquinonedihydrocyanide*, crystallising in laminæ, is formed. The laminar crystals have a higher decomposing point than the acicular. On the other hand, the diacetyl derivative of the laminar compound melts lower than that of the acicular compound. The best yield of the laminar compound is obtained by employing anhydrous hydrocyanic acid.

* See Japp and Miller, Trans., 1887, **51**, 29.

The reactions of the two phenanthraquinonedihydrocyanides show that both have the structural formula $\begin{array}{l}C_6H_4\cdot C(OH)\cdot CN\\ \vert \qquad\;\; \vert \\ C_6H_4\cdot C(OH)\cdot CN\end{array}$. They must therefore be stereoisomerides, the one being the racemic, the other the meso-form, although it is at present impossible to assign to each its specific configuration.

By hydrolysing acicular phenanthraquinonedihydrocyanide, not previously freed from adhering hydrocyanic acid, with fuming hydrochloric acid in the cold, Japp and Miller (*loc. cit.*) obtained two compounds, $C_{15}H_9ON$ (m. p. 241°) and $C_{15}H_{11}O_2N$ (m. p. 183°), both of which yield salts with bases, the former compound taking up water in the process, so that its dehydrated sodium salt, for example, has the formula $C_{15}H_{10}O_2NNa$; but it again parts with water when liberated from its salts, yielding the original compound, $C_{15}H_9ON$ (compare Japp and Miller). From a study of the reactions of these compounds we assign to them the constitutional formulæ

$$\begin{array}{c}\begin{array}{l}C_6H_4\cdot C\cdot CO\\ \vert \qquad \Vert \;\;\; \vert\\ C_6H_4\cdot C\cdot NH\end{array}\\ \text{Phenanthranil}\\ \text{(m. p. 241°).}\end{array} \quad \text{and} \quad \begin{array}{c}\begin{array}{l}C_6H_4\cdot C(OH)\cdot CO\\ \vert \qquad \vert \qquad\quad \vert\\ C_6H_4\cdot CH\text{——}NH\end{array}\\ \text{Hydroxydihydrophenanthranil}\\ \text{(m. p. 183°).}\end{array}$$

Both compounds are capable of interacting also in the tautomeric form, and we are unable to say whether the free substances are lactams, as here represented, or the corresponding lactims. The metallic salts formed from phenanthranil are salts of the unstable phenanthranilic acid, $\begin{array}{l}C_6H_4\cdot C\cdot CO_2H\\ \vert \qquad \Vert\\ C_6H_4\cdot C\cdot NH_2\end{array}$, which, as just mentioned, when liberated from its salts, parts with water, regenerating phenanthranil. Phenanthranil yields a *monacetyl* derivative, $\begin{array}{l}C_6H_4\cdot C\cdot CO\\ \vert \qquad \Vert \;\;\; \vert\\ C_6H_4\cdot C\cdot N\cdot C_2H_3O\end{array}$. Two esters correspond with it: one is *ethyl phenanthranilate*,

$$\begin{array}{l}C_6H_4\cdot C\cdot CO_2C_2H_5\\ \vert \qquad \Vert\\ C_6H_4\cdot C\cdot NH_2\end{array},$$

and the other is the *lactim ester** of phenanthranil, $\begin{array}{l}C_6H_4\cdot C\cdot C\cdot OC_2H_5\\ \vert \qquad \Vert \;\; \Vert\\ C_6H_4\cdot C\cdot N\end{array}$. Both esters, when hydrolysed with sodium hydroxide, yield *sodium phenanthranilate*; but a portion of the lactim ester is transformed, at the same time, into the non-hydrolysable *hydroxyethyldihydrophen-*

* We would suggest that compounds of this type should be called *esters* rather than *ethers*. Thus, in the complex –C(NH)·OAlk of the so-called *imido-ethers*, the imido-group has, structurally, the same function as the doubly-linked oxygen in the complex –CO·OAlk of the ordinary esters, and the name *imido-ester* would indicate more clearly this analogy.

anthranil, $\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ C_6H_4\cdot CH\text{——}N\cdot C_2H_5 \end{array}$, the ethyl group migrating in the process.

Hydroxydihydrophenanthranil, $\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ C_6H_4\cdot CH\text{——}NH \end{array}$, dissolves in sodium carbonate, yielding a sodium salt which is probably

$$\begin{array}{l} C_6H_4\cdot C(OH)\cdot C\cdot ONa \\ C_6H_4\cdot CH\text{——}N \end{array},$$

but was not obtained in a condition suitable for analysis (compare Japp and Miller, *loc. cit.*, p. 35) and which, when its aqueous solution is digested for some time on the water-bath, decomposes, depositing a brown amorphous substance. Acetylated in the cold with acetic anhydride to which a little concentrated sulphuric acid has been added, hydroxydihydrophenanthranil yields a *monacetyl* derivative,

$$\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ C_6H_4\cdot CH\text{——}N\cdot C_2H_3O \end{array},$$

insoluble in sodium carbonate. Treated with sodium ethoxide and ethyl iodide, hydroxydihydrophenanthranil yields the above-mentioned *hydroxyethyldihydrophenanthranil*, $\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ C_6H_4\cdot CH\text{——}N\cdot C_2H_5 \end{array}$, in which the ethyl is doubtless attached to nitrogen, as the compound is not hydrolysed by warming it with alcoholic potassium hydroxide and is moreover insoluble in aqueous caustic alkalis, showing that the labile hydrogen atom has been replaced by ethyl; this ethyl derivative yields a *monacetyl* derivative, $\begin{array}{l} C_6H_4\cdot C(O\cdot C_2H_3O)\cdot CO \\ C_6H_4\cdot CH\text{————}N\cdot C_2H_5 \end{array}$. Warmed with benzaldehyde, hydroxydihydrophenanthranil is converted into a *benzylidene* derivative, probably derived from the lactim form and

$$\begin{array}{c} CH\cdot C_6H_5 \\ \diagup \quad \diagdown \\ O \qquad O \end{array}$$

having the constitution, $\begin{array}{l} C_6H_4\cdot C\text{—}C \\ C_6H_4\cdot CH\cdot N \end{array}$; it would thus be an analogue of chloralide; it is insoluble in caustic alkalis. The foregoing ethyl derivative of hydroxydihydrophenanthranil, as might be expected from its constitution, does not interact with benzaldehyde.

On the other hand, we must point out that sodium phenanthranilate and ethyl phenanthranilate, although, as above formulated, they contain an amino-group, do not interact with benzaldehyde.

At first we were inclined to regard the compound (m. p. 183°), which we have formulated as hydroxydihydrophenanthranil, as phenanthranilic (10-aminophenanthrene-9-carboxylic) acid. This view is, however, untenable, as it would involve the identity of the totally

distinct sodium salts and ethyl esters of the unstable phenanthranilic acid from phenanthranil with those of hydroxydihydrophenanthranil. Besides, there would be no reason why the closed side chain of phenanthranil, when once opened, should spontaneously close again. Nor would such a formula for hydroxydihydrophenanthranil explain the insolubility of the benzylidene and acetyl derivatives of this compound in alkalis, as also the fact that its ethyl derivative is not only insoluble in, but not hydrolysable by, alkalis. It would be necessary, at all events, to assume that phenanthranil and hydroxydihydrophenanthranil contain different hydrocarbon nuclei: that in one of them, possibly the well-known change to the diphenylenemethane nucleus, as in the formation of diphenyleneglycollic acid from phenanthraquinone, has taken place; and, that this is not the case, is shown by the following experiments:

If hydroxydihydrophenanthranil is heated in a sealed tube with fuming hydrochloric acid it yields 9-*hydroxyphenanthrene*,

$$\begin{array}{l} C_6H_4\cdot CH \\ \vert \qquad \Vert \\ C_6H_4\cdot C\cdot OH \end{array},$$

together with the corresponding 9-*phenanthryl oxide*,

$$\begin{array}{l} C_6H_4\cdot CH \quad HC\cdot C_6H_4 \\ \vert \qquad \Vert \qquad\quad \Vert \quad \vert \\ C_6H_4\cdot C{-}O{-}C\cdot C_6H_4 \end{array},$$

and *tetraphenylenefurfuran*, $\begin{array}{l} C_6H_4\cdot C{-\!-}C\cdot C_6H_4 \\ \vert \qquad \Vert \qquad \Vert \quad \vert \\ C_6H_4\cdot C \quad C\, C_6H_4 \\ \qquad\quad \diagdown\diagup \\ \qquad\qquad O \end{array}$, the two last-mentioned compounds being formed from the first (compare Japp and Findlay, Trans., 1897, **71**, 1115). If phenanthranil is treated in the same way, it undergoes the same changes, except that a higher temperature is required owing to the greater stability of the compound. As we were compelled to employ a smaller quantity of phenanthranil for the reaction, we contented ourselves with isolating the primary product—which is also the chief product—9-*hydroxyphenanthrene*.

Both phenanthranil and hydroxydihydrophenanthranil therefore contain the phenanthrene nucleus.

The mechanism of the decomposition may, in the case of phenanthranil, be formulated as follows:

$$\begin{array}{l} C_6H_4\cdot C\cdot CO \\ \vert \qquad \Vert \quad \vert \\ C_6H_4\cdot C\cdot NH \end{array} \xrightarrow{H_2O} \begin{array}{l} C_6H_4\cdot C\cdot CO_2H \\ \vert \qquad \Vert \\ C_6H_4\cdot C\cdot NH_2 \end{array} \longrightarrow \begin{array}{l} C_6H_4\cdot CH \\ \vert \qquad \Vert \\ C_6H_4\cdot C\cdot NH_2 \end{array};$$

then

$$\begin{array}{l} C_6H_4\cdot CH \\ \vert \qquad \Vert \\ C_6H_4\cdot C\cdot NH_2 \end{array} + H_2O + HCl = \begin{array}{l} C_6H_4\cdot CH \\ \vert \qquad \Vert \\ C_6H_4\cdot C\cdot OH \end{array} + NH_4Cl$$

(Japp and Findlay, *loc. cit.*, p. 1117).

We studied the conditions of the hydrolysis of acicular phenanthra-

quinonedihydrocyanide much more thoroughly than had been done by Japp and Miller. A product of the hydrolysis which had been overlooked by them is *diphenylenetartramide*, $\begin{matrix} C_6H_4\cdot C(OH)\cdot CONH_2 \\ | \quad\quad | \\ C_6H_4\cdot C(OH)\cdot CONH_2 \end{matrix}$.

Our attempts to hydrolyse the laminar phenanthraquinone dihydrocyanide were only partially successful, as the reaction does not occur except at a temperature at which the greater part of the substance is resinified. *Phenanthranil* and *hydroxydihydrophenanthranil* were isolated from the product.

Experimental.

Benzildihydrocyanide.

Acetylation of Benzildihydrocyanide.—The benzildihydrocyanide used in this and the following experiments was prepared by Zinin's method as modified by Japp and Miller (Trans., 1887, **51**, 31).

In acetylating the compound, a mixture of 15 grams of acetic anhydride and 4 drops of concentrated sulphuric acid was added to 7 grams of finely-powdered benzildihydrocyanide, and the whole was allowed to stand in the cold for three weeks. The solid was separated by filtration and recrystallised from boiling glacial acetic acid. The yield of recrystallised substance was 6 grams. It crystallised in six-sided plates, or long pointed needles, both of which showed straight extinction, and melted, when rapidly heated, with decomposition at 242°.

Analysis gave figures agreeing with the formula of *diacetylbenzildihydrocyanide*, $\begin{matrix} C_6H_5\cdot C(O\cdot C_2H_3O)\cdot CN \\ | \\ C_6H_5\cdot C(O\cdot C_2H_3O)\cdot CN \end{matrix}$.

0·2079 gave 0·5242 CO_2 and 0·0881 H_2O. C = 68·76 ; H = 4·70.
0·2834 „ 20·05 c.c. moist nitrogen at 8° and 741 mm. N = 8·32.
$C_{20}H_{16}O_4N_2$ requires C = 68·96 ; H = 4·59 ; N = 8·04 per cent.

Action of Concentrated Sulphuric Acid on Benzildihydrocyanide: Formation of Diphenylacetamide, $(C_6H_5)_2CH\cdot CONH_2$.—Forty grams of finely-powdered benzildihydrocyanide were sifted into 400 grams of concentrated sulphuric acid, whilst the mixture was constantly stirred. The whole was allowed to stand for 40 hours, after which it was poured on to pounded ice. The solid substance was separated by filtration and the acid solution was evaporated on the water-bath.

The solid substance was digested with sodium carbonate, which extracted a yellow acid, but in quantity too small for further investigation. The solid residue remaining after this treatment was thoroughly washed with ether, to remove resinous matters. (If the washing with ether has not been sufficient, the residue cannot be induced to crystallise.) The washed residue was recrystallised first

from alcohol, and afterwards from benzene. It was somewhat difficult to purify, but was ultimately obtained in pointed, or obliquely truncated, flat prisms, with an extinction angle of 44—45° from the long axis, and melting at 167·5—168°.

The above-mentioned acid solution yielded, on evaporation, an oil, which solidified on standing. It was boiled with sodium carbonate, and the residue, recrystallised from the foregoing solvents, yielded a further quantity of the substance melting at 167·5—168°. The substance thus obtained was free from resin and was much easier to purify than the original solid residue.

0·2081 gave 0·6048 CO_2 and 0·1181 H_2O. C = 79·26; H = 6·30.
0·2079 „ 0·6041 CO_2 „ 0·1195 H_2O. C = 79·24; H = 6·38.
0·1002 „ 5·95 c.c. moist nitrogen at 20·5° and 759 mm. N = 6·76.
$C_{14}H_{13}ON$ requires C = 79·62; H = 6·16; N = 6·63 per cent.

The compound is *diphenylacetamide*, $(C_6H_5)_2CH\cdot CONH_2$. It was further identified by comparison with a specimen of this substance prepared by heating ammonium diphenylacetate in a sealed tube at 230° (Neure, *Annalen*, 1888, **250**, 141). The melting points, mixture melting point, crystalline form and optical properties of the two preparations were identical. Both Neure, and Anschütz and Römig (*Annalen*, 1886, **233**) give the melting point of diphenylacetamide at 165—166°; but we confirmed the somewhat higher melting point of 167·5—168°, above given, by a determination with a normal thermometer.

The action of hydrochloric acid on benzildihydrocyanide was also studied, but did not yield results of interest. By heating the substance in a sealed tube with fuming aqueous hydrochloric acid the only products obtained were benzoic acid and an uncrystallisable oil. By allowing benzildihydrocyanide to stand with alcoholic hydrogen chloride in the cold, only a hydrochloride of the dihydrocyanide was formed.

*Isomeric Phenanthraquinonedihydrocyanides.**

Acicular Phenanthraquinonedihydrocyanide.—In preparing this compound one of the methods devised by Japp and Miller (*loc. cit.*, p. 33) was employed. Finely powdered phenanthraquinone was allowed to stand for 4—5 days in a strong corked flask with a considerable excess of 30 per cent. aqueous hydrocyanic acid, and the mixture was shaken from time to time. At the end of this time the orange-coloured

* In preparing these compounds, it is essential to employ a phenanthraquinone that has been purified by means of its hydrogen sodium sulphite compound, as otherwise the anthraquinone which is invariably present in specimens of phenanthraquinone which have been purified merely by recrystallisation will contaminate the products.

particles of the phenanthraquinone had disappeared and the flask contained a magma of white, needle-shaped crystals. The substance was freed from the adhering liquid by means of a filter-pump, and then dried in a vacuum desiccator over sulphuric acid. It turns reddish-brown on drying, owing to a partial regeneration of phenanthraquinone.

Japp and Miller purified the substance for analysis by washing it with chloroform, which readily dissolves the phenanthraquinone but in which the dihydrocyanide is practically insoluble. We found, however, that the dihydrocyanide can be recrystallised from hot benzene, provided that too long boiling is avoided. It was deposited in colourless needles, which, when heated in a capillary tube, decompose and turn red at a temperature below 100°.

0·1662 gave 15·1 c.c. moist nitrogen at 13° and 746 mm. N = 10·53

$C_{16}H_{10}O_2N_2$ requires N = 10·69 per cent.

Sometimes the hot benzene solution deposited at first colourless six-sided plates and afterwards needles. We were at first inclined to think that these plates were the stereoisomeric laminar phenanthraquinonedihydrocyanide (to be described later on). On separating some of these plates, however, we found that they showed the same decomposing point as the needles, whereas the laminar form does not decompose until 160—170°, and that their diacetyl derivative melted at 255—256°, the melting point of the diacetyl derivative of the needles, and showed no depression when mixed with a specimen of the latter substance. The difference was, therefore, doubtless nothing more than a difference in crystalline habit.

The following experiments on the loss of weight which acicular phenanthraquinonedihydrocyanide, purified by recrystallisation from benzene, suffers on heating, are of interest. The substance was heated at the respective temperatures until the weight remained constant.

0·6374 lost, on heating at 100° for 2 hours, 0·1314 = 20·61 per cent.

$C_{16}H_{10}O_2N_2 - 2HCN$ requires a loss = 20·61 per cent.

The substance which remained was phenanthraquinone.

0·2102 lost, on heating at 70° for 11 hours (weight constant), 0·0217 = 10·32 per cent.

$C_{16}H_{10}O_2N_2 - HCN$ requires a loss = 10·30 per cent.

The substance which remained in the latter case was a scarlet powder and was doubtless *phenanthraquinonemonohydrocyanide.* Its solution in hot benzene deposited scarlet crystals, but a portion of it was decomposed in the process into phenanthraquinone and hydrocyanic acid.

The experiment just described shows that phenanthraquinonedihydrocyanide, when heated for a long time, shows a much lower decomposing point than that (a little under 100°) indicated by its behaviour when quickly heated in a melting-point tube.

Acetylation of Acicular Phenanthraquinonedihydrocyanide.—Twenty grams of acetic anhydride containing 5 drops of concentrated sulphuric acid were added to 10 grams of powdered acicular phenanthraquinonedihydrocyanide. There was a slight rise of temperature on mixing, and the flask was therefore cooled with water. The dihydrocyanide dissolved completely, and in less than an hour crystals began to form. After two days the contents of the flask had almost solidified to a mass of colourless crystals. After recrystallisation from boiling glacial acetic acid, the substance was obtained in colourless, flat, pointed needles, showing straight extinction and melting, with decomposition, at 255—256°. The yield was 7 grams, and more could be obtained by diluting the acetic anhydride mother liquor with water.

The substance is extraordinarily difficult to burn, and we preferred to determine the carbon and hydrogen in separate portions, using lead chromate for the former and copper oxide for the latter.

0·1838 gave 0·4662 CO_2. C = 69·17.
0·1970 „ 0·4988 CO_2. C = 69·05.
0·1623 „ 0·0617 H_2O. H = 4·22.
0·1568 „ 0·0584 H_2O. H = 4·13.
0·2290 „ 16 c.c. moist nitrogen at 11° and 742·4 mm. N = 8·13.
$C_{20}H_{14}O_4N_2$ requires C = 69·36 ; H = 4·04 ; N = 8·08 per cent.

The compound is therefore the *diacetyl* derivative of acicular phenanthraquinonedihydrocyanide :

$$\begin{array}{l} C_6H_4\cdot C(O\cdot C_2H_3O)\cdot CN \\ | \qquad\quad | \\ C_6H_4\cdot C(O\cdot C_2H_3O)\cdot CN \end{array}$$

Laminar Phenanthraquinonedihydrocyanide.—In the course of an attempt to prepare Japp and Miller's acicular phenanthraquinonedihydrocyanide we employed a much stronger hydrocyanic acid than the 30 per cent. aqueous solution prescribed by them. As very little reaction took place in the cold we heated the mixture of phenanthraquinone and hydrocyanic acid in a stout, corked flask. Most of the phenanthraquinone dissolved, and the solution, on cooling, deposited laminæ, quite different in appearance from the needles of Japp and Miller's compound, and having a much higher decomposing point. The filtrate from the laminæ, as it gave off hydrocyanic acid by exposure to the air, deposited a large quantity of the acicular compound. After various experiments we found that the laminar modification could be best prepared by the following method.

Five grams of finely-powdered phenanthraquinone and 5 grams of anhydrous hydrocyanic acid were heated for 5 hours at 60° in a strong glass tube, of test-tube form and closed by an india-rubber stopper tightly wired. The tube was clamped upright so that only the extreme lower end dipped into a beaker of water heated to the required temperature. In this way a circulation and reflux distillation of the liquid was kept up, and the phenanthraquinone went into solution. On cooling, the liquid deposited colourless, elongated, six-sided laminæ, with bevelled edges, also thick short prisms, of the new compound. After standing for six days in the cold the liquid was decanted from the crystals, which were then washed with 85 per cent. hydrocyanic acid and dried in a vacuum desiccator over sulphuric acid. As the crystals turned brownish on the surface in drying they were washed with chloroform to remove the regenerated phenanthraquinone. The powdered substance dissolved, although with greater difficulty than the acicular modification, in hot benzene, and was deposited in slender, oblique prisms, showing straight extinction. The elongated, six-sided laminæ extinguish at an angle of about 25° from the long axis. When heated, the substance did not decompose until 160—170° (very much higher than the acicular modification), turning red and giving off gas, and finally melting at 200°, the melting point of phenanthraquinone. The original laminæ and thick, short prisms, on the one hand, and the slender prisms from benzene on the other, showed an absolutely identical behaviour in this respect, and all gave the same diacetyl derivative (see next section).

Analysis showed that the compound had the composition of a *phenanthraquinonedihydrocyanide*, $\begin{matrix} C_6H_4\cdot C(OH)\cdot CN \\ | \qquad\quad | \\ C_6H_4\cdot C(OH)\cdot CN \end{matrix}$. It is stereoisomeric with the acicular modification.

0·1559 gave 0·4162 CO_2 and 0·0554 H_2O. C = 72·81 ; H = 3·94.
0·1842 ,, 16·4 c.c. moist nitrogen at 10° and 762 mm. N = 10·69.
0·1850 ,, 17 c.c. moist nitrogen at 14° and 750 mm. N = 10·66.
$C_{16}H_{10}O_2N_2$ requires C = 73·28 ; H = 3·82 ; N = 10·69 per cent.

Analyses I and II were made with the original substance merely washed with chloroform ; analysis III with the substance purified by recrystallisation from benzene.

Both the phenanthraquinonedihydrocyanides are slowly decomposed by the moisture of the air and rapidly on boiling with water or with alcohol. The latter solvent readily dissolves them with evolution of hydrocyanic acid and formation of phenanthraquinone. This decomposition, however, does not occur if the water or the alcohol contains hydrochloric acid.

Acetylation of Laminar Phenanthraquinonedihydrocyanide.—The re-

action was carried out as in the case of the acicular compound (*vide supra*) using the same quantities. The yield of uncrystallised substance was 11 grams. It was deposited from hot glacial acetic acid in long, flat, pointed needles, showing straight extinction, and melting, with decomposition, at 235—237°. It is difficult to burn, and the carbon was determined separately by combustion of the substance in a current of moist oxygen. The figures agreed with the formula of a *diacetyl* derivative, $\begin{array}{l}C_6H_4\cdot C(O\cdot C_2H_3O)\cdot CN\\ |\qquad\quad |\\ C_6H_4\cdot C(O\cdot C_2H_3O)\cdot CN\end{array}$.

0·1549 gave 0·3946 CO_2. C = 69·47.
0·1664 „ 0·0628 H_2O. H = 4·19.
0·2032 „ 14 c.c. moist nitrogen at 9° and 760·5 mm. N = 8·23.
$C_{20}H_{14}O_4N_2$ requires C = 69·36; H = 4·04; N = 8·08 per cent.

The diacetyl derivatives of acicular and laminar phenanthraquinonedihydrocyanide are indistinguishable in appearance and optical properties, so far at least as a rough examination in polarised light is able to decide; but the former melts at 255—256°, the latter at 235—237°, and the mixture of the two at about 220°—in every case with decomposition.

Hydrolysis of the Phenanthraquinonedihydrocyanides.

Hydrolysis of Acicular Phenanthraquinonedihydrocyanide.—Japp and Miller (*loc. cit.*) showed that carbon dioxide is evolved during the formation of phenanthranil and hydroxydihydrophenanthranil by the hydrolysis of acicular phenanthraquinonedihydrocyanide with cold, fuming hydrochloric acid:—

$$C_{16}H_{10}O_2N_2 + H_2O = \underset{\text{Phenanthranil.}}{C_{15}H_9ON} + CO_2 + NH_3,$$

and

$$C_{16}H_{10}O_2N_2 + 2H_2O = \underset{\substack{\text{Hydroxydihydro-}\\ \text{phenanthranil.}}}{C_{15}H_{11}O_2N} + CO_2 + NH_3.$$

As, therefore, the evolution of carbon dioxide may be utilised as an index of the progress of the reaction, we attached, in the majority of the experiments which we made, a delivery tube to the flask in which the hydrolysis was carried out, and collected the carbon dioxide from time to time.

In our first hydrolysis experiment the acicular phenanthraquinonedihydrocyanide, prepared as already described *and dried over sulphuric acid*, was mixed with an excess of the strongest hydrochloric acid and allowed to stand at the ordinary temperature for a fortnight. No gas was given off, and the substance in the flask, freed from hydro-

chloric acid, proved to be unchanged dihydrocyanide. We therefore reverted to Japp and Miller's method, which we describe in detail, inasmuch as the results which we obtained differed somewhat from theirs.

The freshly-prepared hydrocyanide, freed as far as possible from adhering aqueous hydrocyanic acid by means of the filter-pump, *but still moist with this liquid*, was mixed with a large excess of the strongest hydrochloric acid (the ordinary fuming acid into which hydrogen chloride had been passed to complete saturation) in a flask fitted with a delivery tube. Carbon dioxide was evolved and was collected over mercury in a tube containing a little water so as to absorb any hydrogen chloride. Japp and Miller state that the evolution of carbon dioxide ceases "after some days." This is incorrect. The evolution became much slower after about a week, but did not entirely cease until 3½ months had elapsed. The contents of the flask were then diluted with water, and the solid matter was separated by filtration, digested several times on the water-bath with sodium carbonate, and filtered hot. (Too long digestion is to be avoided, as otherwise the sodium salt of hydroxydihydrophenanthranil is decomposed with separation of a brown substance.) After the treatment with sodium carbonate, there was only a small residue which proved to be *diphenylenetartramide* (*vide infra*), whereas Japp and Miller found a large insoluble residue of phenanthraquinone, which must have been regenerated by the action of the hot aqueous carbonate solution on the acicular phenanthraquinonedihydrocyanide that had escaped hydrolysis owing to the shortness of the time during which the experiment was allowed to proceed.*

The united sodium carbonate extracts yielded, on acidification, a copious precipitate, which, after recrystallisation from boiling benzene, was obtained in tufts of slender needles of *hydroxydihydrophenanthranil*, $\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ C_6H_4\cdot CH\text{---}NH \end{array}$, melting at 183°. A small quantity of *phenanthranil*, $\begin{array}{l} C_6H_4\cdot C\cdot CO \\ C_6H_4\cdot C\cdot NH \end{array}$ (m. p. 241°), was obtained from the benzene mother liquor and was freed from any hydroxydihydrophenanthranil with which it was mixed by dissolving it in sodium carbonate and digesting the solution for some days on the water-bath, by which treatment the salt of hydroxydihydrophenanthranil is destroyed with separation of a brown insoluble substance. The filtrate then gives, on acidifying, a precipitate of pure phenanthranil (compare Japp and Miller, *loc. cit.*, p. 36).

Although acicular phenanthraquinonedihydrocyanide that has been

* This residue is not referred to in the original paper.—F. R. J.

previously dried is not hydrolysed by hydrochloric acid in the cold, the reaction readily takes place at a higher temperature.

Seven grams of dry acicular phenanthraquinonedihydrocyanide and 150 c.c. of ordinary fuming hydrochloric acid were heated for 40 hours at 80—90° in a flask fitted with an air condensing tube. The product of the reaction was treated precisely as in the previous experiment; but in the present case phenanthranil was the chief product. It separated in a state of purity from the benzene solution, whilst hydroxydihydrophenanthranil, mixed with phenanthranil, was obtained from the mother liquor.

In this way, by varying the temperature at which the hydrolysis is conducted, one can obtain either phenanthranil or hydroxydihydrophenanthranil as chief product.

Japp and Miller state that phenanthranil and hydroxydihydrophenanthranil are of about equal solubility in benzene. We find, however, that the latter is the more soluble.

We also studied the action of alcoholic hydrogen chloride on acicular phenanthraquinonedihydrocyanide and obtained, in addition to the foregoing compounds, the ethyl ester of phenanthranilic acid and an ethyl derivative of hydroxydihydrophenanthranil.

Twenty-four grams of dry acicular phenanthraquinonedihydrocyanide were mixed with 300 grams of saturated alcoholic hydrogen chloride, and the mixture was allowed to stand for 3 months in a flask fitted with a mercury safety valve. It was noticed that less carbon dioxide was evolved than when aqueous hydrochloric acid was used. The solid substance was separated by filtration, and the alcoholic filtrate was diluted with an equal bulk of water. The solid was treated with water to remove ammonium chloride, and the residue was treated several times with boiling benzene, which extracted phenanthranil mixed with a little hydroxydihydrophenanthranil. The residue from the extraction with benzene was recrystallised from boiling glacial acetic acid, in which it readily dissolved; the crystals were again extracted with benzene, and the residue again recrystallised from glacial acetic acid. The substance was thus obtained in slender transparent prisms melting with decomposition at 274°. It proved to be *diphenylenetartramide* combined with a molecule of acetic acid, the latter being present either as solvent of crystallisation or as salt-forming acid, but probably the former, owing to the ease with which the acetic acid was expelled on heating the compound, and also owing to the fact that the diphenylenetartramide was not found combined with hydrochloric acid in the process in which it was formed. The yield was 0·8 gram. The compound was analysed before we discovered that it contained acetic acid.

0·2040 gave 0·4512 CO_2 and 0·0924 H_2O. C = 60·32 ; H = 5·03.
0·2118 ,, 13·65 c.c. moist nitrogen at 9° and 764·5 mm. N = 7·79.
$C_{16}H_{14}O_4N_2,C_2H_4O_2$ requires C = 60·33 ; H = 5·02 ; N = 7·82 per cent.

The compound was heated at 110° until its weight was constant. It lost 1 mol. proportion of acetic acid.

0·3222 lost, at 110°, 0·0546. Acetic acid = 16·94.
$C_{16}H_{14}O_4N_2,C_2H_4O_2$ requires acetic acid = 16·76 per cent.

The residue melted with decomposition at 274°, like the original substance, as the latter had of course parted with its acetic acid of crystallisation far below this temperature. It was analysed.

0·1342 gave 0·3164 CO_2 and 0·0570 H_2O. C = 64·30 ; H = 4·71.
0·1241 ,, 10·05 c.c. moist nitrogen at 7·5° and 746 mm. N = 9·62.
$C_{16}H_{14}O_4N_2$ requires C = 64·42 ; H = 4·69 ; N = 9·39 per cent.

The compound is, therefore, *diphenylenetartramide*,

$$\begin{array}{l} C_6H_4\cdot C(OH)\cdot CONH_2 \\ | \qquad\;\; | \\ C_6H_4\cdot C(OH)\cdot CONH_2 \end{array}.$$

It is identical with the product obtained by the action of cold fuming hydrochloric acid on acicular phenanthraquinonedihydrocyanide (*vide supra*), as was proved by a comparison of the two specimens and by the mixture melting-point test.

Diphenylenetartramide is not chemically altered by heating with fuming hydrochloric acid at 190—200°, as it merely dissolves in the hot acid and crystallises out again on cooling. It is therefore evident that it cannot be an intermediate product in the formation of phenanthranil and hydroxydihydrophenanthranil.

The phenanthranil obtained by the extraction of the original residue with benzene was freed from hydroxydihydrophenanthranil by destroying the latter compound by digesting the mixture with sodium carbonate for several days on the water-bath as described in the case of the product of the hydrolysis with aqueous hydrochloric acid. It gave the correct melting point of 241°, and was further identified by the mixture melting-point test.

The alcoholic hydrogen chloride filtrate, diluted as already mentioned with water, deposited a solid substance. This was separated by filtration, washed with water, and extracted with hot sodium carbonate, which removed a quantity of hydroxydihydrophenanthranil, which on reprecipitation and recrystallisation from benzene melted at 183°, and was further identified by the mixture melting-point test.

The residue from the foregoing sodium carbonate extraction, recrystallised from benzene, formed very slender white needles melting at 207°. The yield was 0·7 gram.

0·1666 gave 0·4680 CO_2 and 0·0854 H_2O. C = 76·61 ; H = 5·69.
0·2048 „ 9·05 c.c. moist nitrogen at 6° and 741 mm. N = 5·24.
$C_{17}H_{15}O_2N$ requires C = 76·98 ; H = 5·66 ; N = 5·28 per cent.

The synthesis of this compound, to be described later on, from the sodium salt of hydroxydihydrophenanthranil and ethyl iodide, and the fact that it is not hydrolysed by boiling it with alcoholic potassium hydroxide, lead us to regard it as a *hydroxyethyldihydrophenanthranil*, $\begin{matrix} C_6H_4\cdot C(OH)\cdot CO \\ | \quad\quad | \quad\quad\quad | \\ C_6H_4\cdot CH\text{——}N\cdot C_2H_5 \end{matrix}$, in which the ethyl group is attached to nitrogen. Possibly the sodium salt of hydroxydihydrophenanthranil is derived from the tautomeric form and has the formula, $\begin{matrix} C_6H_4\cdot C(OH)\cdot C\cdot ONa \\ | \quad\quad | \quad\quad\quad \| \\ C_6H_4\cdot CH\text{——}N \end{matrix}$, or possibly the side chain opens in the formation of this salt, as in the case of the metallic salts of phenanthranil. Japp and Miller were unable to obtain the metallic salts of hydroxydihydrophenanthranil sufficiently pure to decide with certainty on their composition.

The dilute alcoholic hydrochloric acid filtrate, from which the foregoing substance had been separated by filtration, was allowed to evaporate spontaneously. As the alcohol was given off, a brownish solid was deposited ; this was boiled with benzene, which did not dissolve it, but left it white. This white substance proved to be the hydrochloride of a weak base ; it was found that, by digesting it with water on the water-bath for half an hour, the whole of the hydrochloric acid could be removed. The basic product resulting from this treatment was recrystallised first from alcohol and afterwards from benzene ; from the latter solvent it is deposited in slender needles with a yellowish tinge, melting at 185°, with decomposition, to a red liquid which resolidifies and then does not melt even at 290°.

0·1485 gave 0·4171 CO_2 and 0·0742 H_2O. C = 76·60 ; H = 5·55.
0·1868 „ 8·45 c.c. moist nitrogen at 9° and 733 mm. N = 5·24.
$C_{17}H_{15}O_2N$ requires C = 76·98 ; H = 5·66 ; N = 5·28 per cent.

We regard this compound as *ethyl phenanthranilate* (10-*aminophenanthrene*-9-*carboxylate*), $\begin{matrix} C_6H_4\cdot C\cdot CO_2C_2H_5 \\ | \quad\quad \| \\ C_6H_4\cdot C\cdot NH_2 \end{matrix}$, although we must point out that the fact that the substance does not interact with benzaldehyde, even at the boiling point of the latter, is not in keeping with this formula.

When the foregoing ester (m. p. 185°) is heated with aqueous caustic soda, it dissolves, and on acidifying the solution, phenanthranil is precipitated, the liberated phenanthranilic acid parting with water and yielding this compound. The phenanthranil thus obtained was recrystallised from benzene. It showed the correct melting point of 241° and was further identified by the mixture melting-point test.

By treating the foregoing ester (m. p. 185°) in the cold with excess of acetic anhydride containing a little concentrated sulphuric acid (1 drop per 5 grams), a crystalline substance was obtained, insoluble in the ordinary organic menstrua, melting at 218—219°, and yielding, on analysis, C = 76·55, H = 4·47, N = 5·05. These figures do not appear to lead to any formula that can be accounted for. Possibly the carbon is too low, but we had not sufficient substance for further analysis.

An attempt to synthesise the foregoing ester (m. p. 185°) from sodium phenanthranilate and ethyl iodide yielded, instead, *phenanthranil ethyl ester*, $\begin{array}{l} C_6H_4\cdot C\cdot C\cdot OC_2H_5 \\ C_6H_4\cdot C\cdot N \end{array}$ (m. p. 110°), derived from the lactim form of phenanthranil (*vide infra*).

Hydrolysis of Laminar Phenanthraquinonedihydrocyanide.—In the case of this substance only the hydrolysis with aqueous hydrochloric acid was studied. At the ordinary temperature fuming hydrochloric acid had no action whatever. It was necessary to heat the finely-powdered substance with the fuming acid at 100° in order to obtain any result. Only a small quantity of *phenanthranil* and *hydroxydihydrophenanthranil* could be isolated from the product. Dark-coloured, resinous matters, insoluble in sodium carbonate, were formed in considerable amount.

Hydroxydihydrophenanthranil,

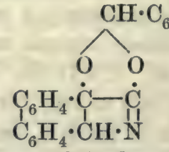
$$\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ C_6H_4\cdot CH\text{——}NH \end{array} \quad \text{or} \quad \begin{array}{l} C_6H_4\cdot C(OH)\cdot C\cdot OH \\ C_6H_4\cdot CH\text{——}N \end{array} \quad \text{(m. p. 183°).}$$

Acetylhydroxydihydrophenanthranil, $\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ C_6H_4\cdot CH\text{——}N\cdot C_2H_3O \end{array}$ (m. p. 190—192°, with decomposition).—One gram of hydroxydihydrophenanthranil, 6 grams of acetic anhydride, and 1 drop of concentrated sulphuric acid were allowed to interact in the cold for 3 weeks. The solid was filtered off, washed with a little cold glacial acetic acid, and recrystallised from boiling alcohol. It forms small white needles melting at 190—192° with decomposition. The yield was almost 1 gram.

0·1826 gave 0·4904 CO_2 and 0·0792 H_2O. C = 73·24 ; H = 4·81.
0·1460 „ 6·2 c.c. moist nitrogen at 6° and 751 mm. N = 5·10.
$C_{17}H_{13}O_3N$ requires C = 73·11 ; H = 4·65 ; N = 5·01 per cent.

The compound is therefore a *monacetyl* derivative of hydroxydihydrophenanthranil. The acetyl group replaces the labile hydrogen atom, as the compound does not dissolve in sodium carbonate. On long digestion with sodium carbonate solution on the water-bath, however, it is decomposed with separation of the brown amorphous substance which hydroxydihydrophenanthranil yields under similar

circumstances, the decomposition being, in the present case, doubtless preceded by the hydrolysis of the acetyl derivative.

Benzylidenehydroxydihydrophenanthranil,  (m. p. 245—246° with decomposition).—Half a gram of hydroxydihydrophenanthranil was boiled for 3 minutes in a test-tube with 2 grams of benzaldehyde. Water was given off. Alcohol was then added and the mixture digested for some time. The crystalline substance which separated was recrystallised from boiling glacial acetic acid, from which it was deposited in clusters of very slender white needles melting at 245—246° with decomposition, evolving gas and turning yellow. It is very sparingly soluble in alcohol and in benzene, and does not dissolve in sodium carbonate or sodium hydroxide even on long heating.

0·1702 gave 0·5018 CO_2 and 0·0728 H_2O. C = 80·40; H = 4·75.
0·2585 „ 9·35 c.c. moist nitrogen at 7° and 756 mm. N = 4·36.
$C_{22}H_{15}O_2N$ requires C = 81·23; H = 4·61; N = 4·30 per cent.

The compound is thus the *benzylidene* derivative of hydroxydihydrophenanthranil.

Phenanthranil, on the contrary, is not acted on by benzaldehyde at the boiling point of the latter.

Synthesis of Hydroxyethyldihydrophenanthranil,

$$\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ C_6H_4\cdot CH\text{——}N\cdot C_2H_5 \end{array}$$

(m. p. 207°).—As the salts of hydroxydihydrophenanthranil are very unstable, we thought it better, instead of attempting to prepare its sodium salt and acting on this with ethyl iodide, to employ the method of alkylation devised by Japp and Klingemann (Trans., 1888, **53**, 526—527) to meet such cases.

One and a half grams of hydroxydihydrophenanthranil and 4·8 grams of ethyl iodide were dissolved in absolute ethyl alcohol, the solution was boiled in a flask fitted with a reflux condenser, and a solution of 0·7 gram of sodium in absolute alcohol was allowed to fall drop by drop into the boiling liquid. The boiling was continued for $3\frac{1}{2}$ hours. The solution was cooled, diluted with water, and extracted with ether. The ethereal extract was freed from a small quantity of unchanged hydroxydihydrophenanthranil by shaking it with sodium carbonate solution, and a further quantity of the same compound was precipitated on acidifying the extracted aqueous alcoholic solution, 0·4 gram of unchanged substance in all being thus recovered. The ethereal extract yielded, on evaporation, *hydroxy-*

ethyldihydrophenanthranil, which crystallised from boiling benzene in slender, white needles melting at 207°. It was proved by the mixture melting-point test to be identical with the substance of the same melting point obtained by the action of alcoholic hydrogen chloride on acicular phenanthraquinonedihydrocyanide.

0·2000 gave 0·5633 CO_2 and 0·1029 H_2O. C = 76·77 ; H = 5·71.

$C_{17}H_{15}O_2N$ requires C = 76·98 ; H = 5·66.

As already mentioned, the compound is not hydrolysed by boiling it with alcoholic potassium hydroxide. We also ascertained that boiling benzaldehyde is without action on it.

Acetyl Derivative of Hydroxyethyldihydrophenanthranil,

$$\begin{array}{l} C_6H_4\cdot C(O\cdot C_2H_3O)\cdot CO \\ C_6H_4\cdot CH\text{———————}N\cdot C_2H_5 \end{array}$$

(m. p. 148—149°).—One gram of hydroxyethyldihydrophenanthranil (m. p. 207°), 10 grams of acetic anhydride, and 1 drop of concentrated sulphuric acid were allowed to stand in the cold. At first the substance dissolved, but afterwards the liquid became filled with crystals. At the end of a fortnight the solid was separated by filtration; the filtrate, diluted with water, yielded a further quantity of the same product, the total yield being 0·8 gram. The substance was purified by dissolving it in benzene and adding light petroleum, when it separates in very slender, silky needles melting constantly at 148—149°.

0·1674 gave 0·4548 CO_2 and 0·0847 H_2O. C = 74·09 ; H = 5·62.

0·2544 „ 10·00 c.c. moist nitrogen at 15·5° and 756 mm. N = 4·56.

$C_{19}H_{17}O_3N$ requires C = 74·26 ; H = 5·53 ; N = 4·56 per cent.

Hydrolysis of Hydroxydihydrophenanthranil with Fuming Hydrochloric Acid.—Three sealed tubes, each containing 2 grams of hydroxydihydrophenanthranil with 50 c.c. of fuming hydrochloric acid, were heated for 6 hours at 130°. There was pressure in the tubes on opening. The fused mass of organic substance was powdered and extracted with ether. The ethereal solution was shaken with dilute sodium hydroxide, and the sodium hydroxide solution, heated to expel ether and then filtered, was saturated with carbon dioxide. A phenolic substance was thus precipitated which, after recrystallisation from hot benzene, formed brownish needles melting at 151—153°. The properties were those of *9-hydroxyphenanthrene*, $\begin{array}{l} C_6H_4\cdot CH \\ C_6H_4\cdot C\cdot OH \end{array}$, and its melting point was not altered by mixing it with a specimen of this compound prepared by Japp and Klingemann (Trans., 1893, 63, 770) by the partial reduction of phenanthraquinone with hydriodic acid.

0·1601 gave 0·5051 CO_2 and 0·0751 H_2O. C = 86·04 ; H = 5·21.

$C_{14}H_{10}O$ requires C = 86·60 ; H = 5·16 per cent.

It was further identified by mixing its hot benzene solution with a similar solution of phenanthraquinone. The mixed solution deposited, on cooling, ruby-red, lozenge-shaped crystals of the compound $C_{28}H_{18}O_3$, melting at 155° (compare Japp and Findlay, 1897, 71, 1121).

The ethereal solution from which the 9-hydroxyphenanthrene had been removed by sodium hydroxide yielded, on evaporation, a substance, which, after recrystallisation from benzene, formed crystals melting at 209°. This proved to be 9-*phenanthryl oxide*,

$$\begin{array}{l} C_6H_4\cdot CH \quad HC\cdot C_6H_4 \\ C_6H_4\cdot C{-}O{-}C\cdot C_6H_4 \end{array}$$

(m. p. 210°).

It was identified by a comparison, including the mixture melting-point test, with the original specimen of this substance prepared by Japp and Findlay (*loc. cit.*, p. 1119). Examined microscopically, both specimens appeared as rhomboidal plates with an acute angle of about 66° and with extinction parallel to the diagonal.

The residue, which remained after the extraction of the original product of hydrolysis with ether, was recrystallised from boiling coal oil (b. p. 170—190°). It was thus obtained in clusters of colourless slender needles melting at 305° and was identified as *tetraphenylene-furfuran*, $\begin{array}{l} C_6H_4\cdot C{-\!-}C\cdot C_6H_4 \\ C_6H_4\cdot C \quad\; C\cdot C_6H_4 \\ \qquad\quad \diagdown\!\diagup \\ \qquad\quad\; O \end{array}$, both by the mixture melting-point test and by the colour reaction with concentrated sulphuric acid and sodium nitrite (compare Japp and Findlay, *loc. cit.*, p. 1120).

Phenanthranil,

$$\begin{array}{l} C_6H_4\cdot C\cdot CO \\ C_6H_4\cdot C\cdot NH \end{array}, \text{ or } \begin{array}{l} C_6H_4\cdot C\cdot C\cdot OH \\ C_6H_4\cdot C\cdot N \end{array} \quad \text{(m. p. 241°)}.$$

Acetylphenanthranil, $\begin{array}{l} C_6H_4\cdot C\cdot CO \\ C_6H_4\cdot C\cdot N\cdot C_2H_3O \end{array}$ (m. p. 145°).—The acetylation was carried out with acetic anhydride containing a small quantity of concentrated sulphuric acid, exactly as in the acetylation of hydroxydihydrophenanthranil (*vide supra*) and using the same proportions. The product was crystallised from hot alcohol, in which it is readily soluble. It formed clusters of slender, silky needles melting at 145°. It does not dissolve in sodium carbonate solution, even at 100°. Analysis showed that a *monacetyl* derivative had been formed.

0·1634 gave 0·4660 CO_2 and 0·0624 H_2O. C = 77·77 ; H = 4·24.
0·1716 „ 0·4930 CO_2 „ 0·0666 H_2O. C = 78·35 ; H = 4·31.
0·2186 „ 9·05 c.c. moist nitrogen at 6° and 759 mm. N = 5·03.
$C_{17}H_{11}O_2N$ requires C = 78·16 ; H = 4·21 ; N = 5·36 per cent.

Lactim Ester of Phenanthranil (*Phenanthranil Ethyl Ester*),

$$\begin{array}{l} C_6H_4{\cdot}C{\cdot}C{\cdot}O\ {}_2H_5 \\ C_6H_4{\cdot}C{\cdot}N \end{array}$$

(m. p. 110°).—Sodium phenanthranilate, $\begin{array}{l} C_6H_4{\cdot}C{\cdot}CO_2Na \\ C_6H_4{\cdot}C{\cdot}NH_2 \end{array}$,$4H_2O$, was prepared by dissolving phenanthranil in a hot solution of sodium carbonate; on cooling, the liquid deposited laminæ of the salt. It was dried at 110° to expel water of crystallisation. The dried salt, together with an excess of ethyl iodide, was dissolved in absolute alcohol, and the mixture was boiled for 3½ hours. Dilution with water precipitated a white substance; this was filtered off and digested with warm sodium carbonate, which removed a little phenanthranil. The residue was recrystallised, first from alcohol and afterwards from light petroleum (sp. gr. 0·71—0·72). It was thus obtained in slender needles melting at 110°. It is very soluble both in alcohol and in benzene.

0·1342 gave 0·4064 CO_2 and 0·0662 H_2O. C = 82·59 ; H = 5·48.
0·2256 „ 11·25 c.c. moist nitrogen at 11·5° and 758 mm. N = 5·92.
$C_{17}H_{13}ON$ requires C = 82·59 ; H = 5·26 ; N = 5·66 per cent.

An attempt to acetylate the compound with acetic anhydride containing a little sulphuric acid gave no result.

A portion of the compound was digested on the water-bath in a silver basin with a 20 per cent. solution of potassium hydroxide in absolute alcohol, renewing the alcohol as required. The alcohol was then expelled, water was added, and the mixture was digested and filtered hot from the insoluble residue. The hot filtrate was acidified and the precipitate recrystallised from benzene. Needles of *phenanthranil* (m. p. 241°) were thus obtained. The insoluble residue, separated by filtration from the potassium hydroxide solution, was crystallised from benzene; it was thus obtained in slender needles melting at 207°, and was identical with the *hydroxyethyldihydrophenanthranil*, $\begin{array}{l} C_6H_4{\cdot}C(OH){\cdot}CO \\ C_6H_4{\cdot}CH\text{——}N{\cdot}C_2H_5 \end{array}$, already described, as was proved by the mixture melting-point test. The lactim ester of phenanthranil is thus partly hydrolysed to phenanthranil, and partly transformed by migration of the ethyl group and assumption of the elements of water into hydroxyethyldihydrophenanthranil.

The latter result was so surprising that we repeated the entire

experiment, preparing the lactim ester of phenanthranil from a specimen of phenanthranil which had been purified by digesting it for several days on the water-bath with a solution of sodium carbonate and from which, consequently, every trace of hydroxydihydrophenanthranil must have been removed by the destruction of this compound. The result, however, was the same as before.

The only alternative, so far as we can see, to assuming a migration of the ethyl group from carbon to nitrogen in a portion of the lactim ester is to suppose that the latter substance is in reality a mixture of the *O*-ethyl and *N*-ethyl derivatives of phenanthranil, the former being hydrolysed by the caustic alkali to phenanthranil, and the latter taking up the elements of water to form the hydroxyethyldihydrophenanthranil. The lactim ester of phenanthranil, however, shows no sign of being other than a perfectly homogeneous substance.

We also digested a specimen of hydroxyethyldihydrophenanthranil (m. p. 207°), prepared from hydroxydihydrophenanthranil, ethyl iodide, and sodium ethoxide (*vide supra*), for $3\frac{1}{2}$ hours with 20 per cent. alcoholic potassium hydroxide on the water-bath. The hydroxyethyldihydrophenanthranil was recovered unchanged, and the potash solution, treated as in the experiment just described, gave no precipitate on acidifying.

Hydrolysis of Phenanthranil with Fuming Hydrochloric Acid.—Unlike hydroxydihydrophenanthranil, phenanthranil is not acted on by fuming hydrochloric acid at 130°. At a temperature of 160—170°, however, 9-*hydroxyphenanthrene* was formed, and was identified by its properties and by the mixture melting-point test. As the quantity of phenanthranil which we could spare for the experiment was small, we did not search for the other products obtained from hydroxydihydrophenanthranil.

The production of 9-hydroxyphenanthrene, both from phenanthranil and from hydroxydihydrophenanthranil, is of importance, inasmuch as it proves, as already pointed out, that both these compounds contain the phenanthrene nucleus.

Distinction between Phenanthranil (m. p. 241°) *and Hydroxydihydrophenanthranil* (m. p. 183°).—Both phenanthranil and hydroxydihydrophenanthranil crystallise from benzene in slender needles, the former being the less soluble. The two substances are very similar in appearance. In addition to the melting points, the following differences may be noted. In polarised light the needles of phenanthranil show straight extinction; those of hydroxydihydrophenanthranil oblique extinction at an angle of about 13° from the long axis. Phenanthranil does not dissolve in cold concentrated sulphuric acid, but, on warm-

ing, dissolves slowly, yielding a grass-green solution. Hydroxydihydrophenanthranil dissolves in cold concentrated sulphuric acid giving a light yellow solution which is unaltered on warming.

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A Condensation Product of Mandelonitrile.

By FRANCIS ROBERT JAPP, F.R.S., and JOSEPH KNOX, B.Sc., Carnegie Scholar in the University of Aberdeen.

BY saturating a solution of mandelonitrile (benzaldehydecyanhydrin) in absolute ether with gaseous hydrogen chloride, Minovici (*Ber.*, 1899, **32**, 2206) obtained a yellow compound of the formula $C_{16}H_{12}ON_2$:—

$$2C_6H_5\cdot CH(OH)\cdot CN = C_{16}H_{12}ON_2 + H_2O.$$

Minovici found the melting point of this substance at 200—203°. It was not hydrolysed by heating either with potassium hydroxide or with hydrochloric acid. It formed an unstable hydrochloride, which was at once decomposed in contact with water or alcohol, liberating the base. The author suggests, as a possible constitution,

$$C_6H_5\cdot CH(CN)\cdot C(OH)(CN)\cdot C_6H_5,$$

but admits that this formula is not in keeping with the reactions of the compound.

Minovici has failed to notice that this compound is identical with a substance which Japp and Miller (Trans., 1887, **51**, 29) obtained, along with other products, by dissolving benzil in alcohol, adding a considerable excess of anhydrous hydrocyanic acid, and saturating the liquid with gaseous hydrogen chloride. They point out that the compound contains in its molecule an atom of oxygen less than benzildihydrocyanide:

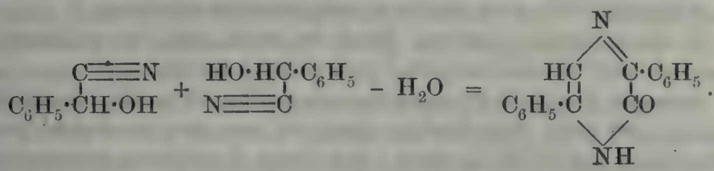
$$C_{16}H_{12}O_2N_2 = C_{16}H_{12}ON_2 + O,$$

but they were unable to prepare the substance by the action of alcoholic hydrogen chloride on pure benzildihydrocyanide. They found the melting point at 196—197°. The yield was very small.

Minovici's reaction explains the mode of formation of this substance in the process described by Japp and Miller. Under the influence of the alcoholic hydrocyanic acid a portion of the benzil is converted into a mixture of benzaldehyde and ethyl benzoate (compare Michael and Palmer, *Amer. Chem. J.*, 1885, **7**, 189); and the benzaldehyde then interacts with the hydrocyanic acid to form mandelonitrile, which is finally transformed by the hydrogen chloride into the compound $C_{16}H_{12}ON_2$, as in Minovici's reaction. The formation of ethyl benzoate was observed by Japp and Miller (*loc. cit.*).

A careful comparison of the substance obtained by Minovici's method with one of Japp and Miller's original preparations showed that the two were identical. We confirmed in both cases the melting point 196—197° given by Japp and Miller. Minovici gives 200—203°.

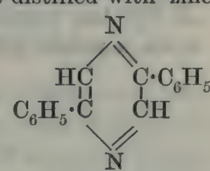
The reactions of the compound lead us to regard it as 3-*keto*-2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*, formed according to the scheme



It is somewhat difficult to give an account of the precise mechanism of the process in which the substance is produced, and we therefore confine ourselves to stating the reaction in the foregoing summary form.

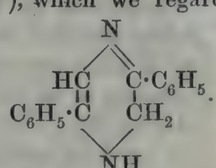
The ketonic formula appears more probable than the tautomeric enolic form, because the former accounts better for the facts (1) that the compound cannot be acetylated, and (2) that, when it is reduced with hydriodic acid, the oxygen atom is replaced by 2 atoms of hydrogen; whereas, if a hydroxyl group were replaced by a hydrogen atom, the resulting diazine would not be further reduced. As regards the latter point, Staedel and Kleinschmidt, it is true, claim to have reduced 2 : 5-diphenyl-1 : 4-diazine ("*iso*indole") by the action of hydriodic acid to a yellow, basic compound (*Ber.*, 1878, 11, 1746); but we have entirely failed to confirm this result (*vide infra*).

We find that when the condensation compound is distilled with zinc dust, it is reduced to 2 : 5-*diphenyl*-1 : 4-*diazine*,



(m. p. 194—195°), a compound first obtained by Staedel and Rügheimer by the action of ammonia on ω-chloroacetophenone (*Ber.*, 1876, 9, 563), but of which the correct composition and constitution were ascertained later by L. Wolff (*Ber.*, 1887, 20, 432).*

If, on the other hand, the condensation compound is reduced by heating it with hydriodic acid and red phosphorus, it yields a compound of the formula $C_{16}H_{14}N_2$ (m. p. 162—163°), which we regard as 2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*,



* Wolff, however, in accordance with the view at that time prevailing on the subject of the constitution of diazines of this type, formulated the compound with a para-bond between the two nitrogen atoms.

That it is not a 1 : 4-dihydro-compound is indicated by the fact that on distillation it does not part with hydrogen yielding 2 : 5-diphenyl-1 : 4-diazine. We were unable to acetylate this substance.

Of the numerous reactions which we tried with the condensation product, only the two foregoing gave positive results.

Attempts to obtain the condensation product by acting on mandelonitrile with other dehydrating agents did not give the desired result. Thus acetic anhydride to which a few drops of sulphuric acid had been added converted mandelonitrile in the cold, with liberation of hydrocyanic acid, into a compound melting at 239—240° and having the formula $C_{27}H_{26}O_6N_2$. The yield of this substance is greatly increased by previously adding to the mandelonitrile half its molecular proportion of benzaldehyde. It is formed according to the equation:

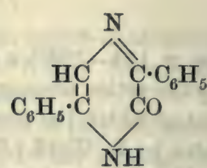
$$2C_6H_5{\cdot}CH(OH){\cdot}CN + C_6H_5{\cdot}CHO + (C_2H_3O)_2O = C_{27}H_{26}O_6N_2,$$

and its constitution may be represented by the formula

$$C_6H_5{\cdot}CH[NH{\cdot}CO{\cdot}CH(O{\cdot}C_2H_3O){\cdot}C_6H_5]_2.$$

The reaction in which it is formed is thus analogous to that discovere by Hepp and Spiess (*Ber.*, 1876, 9, 1425) in which acetaldehyde and benzonitrile, under the influence of concentrated sulphuric acid, yield ethylidenedibenzamide, $CH_3{\cdot}CH(NH{\cdot}CO{\cdot}C_6H_5)_2$. Heated with water at 180° the compound $C_{27}H_{26}O_6N_2$ was hydrolysed, yielding benzaldehyde, mandelic acid and acetic acid.

EXPERIMENTAL.

3-*Keto*-2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*, 

(m. p. 196—197°).

Comparison of the Compound $C_{16}H_{12}ON_2$ *obtained by Minovici's Method with that described by Japp and Miller.*—We prepared a quantity of the compound $C_{16}H_{12}ON_2$ by Minovici's method of saturating a solution of mandelonitrile in *absolute* ether with gaseous hydrogen chloride (*Ber.*, 1899, 32, 2206). The product was purified by boiling it in alcoholic solution with animal charcoal and afterwards recrystallising it repeatedly from alcohol. It was compared with a specimen of the substance of the same formula prepared by Japp and Miller from benzil by the method already described.

Both preparations melted at 196—197°, and showed no depression of melting point when mixed. Both crystallised in flat, pointed, lustrous, yellow needles showing straight extinction. Both dissolved in concentrated sulphuric acid giving an orange-yellow coloration. They were therefore identical.

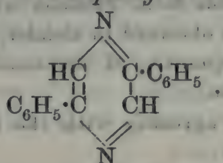
Both products had been previously analysed by their discoverers.

We have already given our reasons for assigning to the compound the constitution of a *3-keto-*2 : 5*-diphenyl-*3 : 4*-dihydro-*1 : 4*-diazine.*

As, of the two methods for preparing the compound, that of Minovici is both the simpler and gives the better—although a far from satisfactory—yield, it was employed in obtaining the material required for the following reactions.

The compound could not be acetylated either by boiling it for several hours with excess of a mixture of acetic anhydride and anhydrous sodium acetate, or by allowing it to stand in the cold with acetic anhydride containing a few drops of concentrated sulphuric acid, nor did it yield a nitroso-derivative on adding solid sodium nitrite to its solution in glacial acetic acid.

Distillation of the Compound $C_{16}H_{12}ON$ (m. p. 196—197°) *with Zinc Dust: Formation of* 2 : 5*-Diphenyl-*1 : 4*-diazine,*

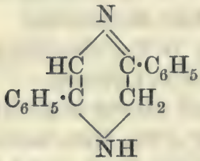


—Eight grams of the compound $C_{16}H_{12}ON_2$ were distilled with zinc dust in four portions—2 grams of substance mixed with 20 grams of zinc dust being used for each distillation. The united alcoholic extracts of the distillates were concentrated, and the solution was nucleated with a trace of dust of 2 : 5-diphenyl-1 : 4-diazine, prepared by the action of alcoholic ammonia on ω-bromoacetophenone (Staedel and Kleinschmidt, *Ber.*, 1880, **13**, 836; compare also Braun and Victor Meyer, *Ber.*, 1888, **21**, 1279). The impure crystalline substance which was thus deposited was washed with cold ether and recrystallised thrice from boiling alcohol. It melted constantly at 194—195°. The quantity was unfortunately too small for analysis, but, as the properties of the substance pointed to its being 2 : 5-diphenyl-1 : 4-diazine, we identified it by comparison with a specimen of the latter compound prepared by Staedel and Kleinschmidt's method just referred to. Both preparations consisted of yellow, lustrous crystals, which, under the microscope, appeared as broad, flat, pointed prisms showing straight extinction, or four-sided plates, frequently overlapping, extinguishing parallel to the diagonal. Both melted at 194—195°, and, when mixed together, showed no depression of melting point. Both

dissolved in concentrated sulphuric acid with a reddish-yellow colour, and were precipitated on diluting the solution with water.

The substance is therefore 2 : 5-*diphenyl*-1 : 4-*diazine*.

Reduction of the Compound $C_{16}H_{12}ON_2$ (m. p. 196—197°) *with Hydriodic Acid: Formation of* 2 : 5-*Diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*,



.—Two grams of the compound $C_{16}H_{12}ON_2$, 20 grams of hydriodic acid (sp. gr. 1·7), and 0·5 gram of red phosphorus were heated in a sealed tube at 200° for 6 hours. There was great pressure on opening the tube, which contained a brittle black mass. The contents of the tube were diluted with water, the acid liquid was decanted, and the remaining black solid was shaken with ether, in which it entirely dissolved. The ethereal solution was shaken with an aqueous solution of sulphur dioxide, which caused the separation of a brown oil; this was run off; it solidified on standing. The solid was digested on the water-bath with a solution of sodium carbonate, and purified by crystallisation from benzene with the addition of light petroleum. It was thus obtained in slender, white needles melting at 162—163°. A further quantity of the same compound was obtained from the ethereal solution.

Analysis gave figures agreeing with the formula of 2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*:—

0·1792 gave 0·5349 CO_2 and 0·0985 H_2O. C = 81·40 ; H = 6·10.
0·2569 „ 25·6 c.c. moist nitrogen at 13° and 770 mm. N = 11·94.
$C_{16}H_{14}N_2$ requires C = 82·05 ; H = 5·98 ; N = 11·96 per cent.

In a previous reduction experiment in which the same proportions were employed and the tube was also heated for 6 hours, but at a temperature of only 150°, there was obtained, along with the foregoing product, a substance which crystallised from benzene, on addition of light petroleum, in slender, white needles melting at 182—184°. It contained iodine, which was not removed on adding aqueous sodium hydroxide to an alcoholic solution of the substance. It was not further examined.

2 : 5-Diphenyl-3 : 4-dihydro-1 : 4-diazine was distilled under reduced pressure in the hope that it might part with hydrogen and yield 2 : 5-diphenyl-1 : 4-diazine ; but only unchanged substance could be isolated from the distillate.

An attempt to acetylate it by allowing it to stand at the ordinary temperature with acetic anhydride to which a few drops of sulphuric

acid had been added, also led to no result. The substance was recovered unchanged.

Attempt to reduce 2 : 5-*Diphenyl*-1 : 4-*diazine*.—Staedel and Kleinschmidt (*Ber.*, 1878, **11**, 1746) state that "*iso*indole" (2 : 5-diphenyl-1 : 4-diazine) can be reduced with hydriodic acid to a yellow basic compound melting at 125° which yields an acetyl derivative crystallising in clear yellow needles melting at 190°. No analyses are given, and, so far as we can discover, nothing further has ever been published on the subject.

In view of the well-known difficulty of reducing paradiazines, we thought it of interest to test the correctness of the foregoing statements. We therefore heated 2 : 5-diphenyl-1 : 4-diazine (prepared by the action of alcoholic ammonia on ω-bromoacetophenone) with excess of hydriodic acid (sp. gr. 1·7) and red phosphorus for 6 hours at 200°. The tube contained a dark mass, from which we succeeded in isolating a very small quantity of a yellowish-brown, non-basic oil, which could not be induced to crystallise. Nearly the whole of the diazine was recovered unchanged.

Action of Acetic Anhydride containing a little Sulphuric Acid on a Mixture of Benzaldehyde and Mandelonitrile.—In the first experiment in which the substance about to be described was obtained, no benzaldehyde was added to the mixture, a part of the mandelonitrile breaking up in the process into benzaldehyde and hydrocyanic acid. By adding benzaldehyde to start with, the yield is greatly increased.

Ten grams of benzaldehyde and 25 grams of mandelonitrile were mixed and slowly added to 35 c.c. of acetic anhydride containing 7 drops of concentrated sulphuric acid. On standing for some time the mixture deposited slender needles, the quantity of which gradually increased. At the end of six weeks the mixture was poured into water and digested on the water-bath, first with water, then with a solution of sodium carbonate, and finally with a little alcohol. The white residue was then recrystallised from boiling glacial acetic acid, in which it is moderately soluble. It was thus obtained in slender, colourless needles, showing straight extinction and melting constantly at 239—240°. The substance has the constitution

$$C_6H_5\cdot CH[NH\cdot CO\cdot CH(O\cdot C_2H_3O)\cdot C_6H_5]_2.$$

0·1468 gave 0·3661 CO_2 and 0·0724 H_2O. C = 68·01 ; H = 5·48.
0·3102 „ 15·8 c.c. moist nitrogen at 15° and 768 mm. N = 6·03.
$C_{27}H_{26}O_6N_2$ requires C = 68·35 ; H = 5·48 ; N = 5·92 per cent.

A quantity of this substance was heated with water in a sealed tube at 180° for 8 hours. The organic products of hydrolysis were

benzaldehyde, mandelic acid, and acetic acid. The benzaldehyde was identified by its smell, and by converting it into benzalazine (m. p. 93°); the mandelic acid by the mixture melting-point test; and the acetic acid by the ethyl acetate reaction.

We have to thank the Council of the Royal Society for an allotment from the Government Grant in aid of the work described in this and the two preceding papers.

CHEMICAL DEPARTMENT,
UNIVERSITY OF ABERDEEN.

Action of Hydrazine on Unsaturated γ-Diketones.

By Francis Robert Japp, F.R.S., and James Wood, M.A., B.Sc., Carnegie Scholar in the University of Aberdeen.

C. Paal and Heinrich Schulze (*Ber.*, 1900, 33, 3796) have shown that the *cis*- and *trans*-forms of *s*-dibenzoylethylene,

$$C_6H_5 \cdot CO \cdot CH \colon CH \cdot CO \cdot C_6H_5,$$

may be readily distinguished from one another by the greater ease with which the *cis*-form interacts with hydrazine to form a 1 : 2-diazine.

We have employed this reaction to ascertain the configurations of some analogous unsaturated γ-diketones: *αβ*-dibenzoylstyrene, dibenzoylstilbene, and *α*-benzoyl-*β*-trimethacetylstyrene. In the case of the last-mentioned compound, only one form is known; but the ease with which it forms a diazine shows that it has the *cis*-configuration. The result in the case of dibenzoylstyrene and dibenzoylstilbene has been to confirm the configurations assigned to the different modifications of these compounds by Japp and Klingemann (Trans., 1890, 57, 667):

	cis-Form.	*trans*-Form.
αβ-Dibenzoylstyrene	m. p. 129°	m. p. 197—198°.
Dibenzoylstilbene	m. p. 220°	m. p. 232°.

The *cis*-forms of these compounds do not yield the corresponding diazines so readily as *cis*-*s*-dibenzoylethylene—doubtless owing to their higher molecular weight and consequent greater inertness; and, for the same reason, their *trans*-forms do not interact with hydrazine at all, whereas *trans*-dibenzoylethylene differs from the *cis*-form, as already mentioned, only in the greater difficulty with which the formation of the diazine takes place. In the reactions which we are about to describe, a reducing action of the hydrazine sometimes accompanies the formation of the diazine, so that dibenzoylstyrene yields, at least when the reaction is allowed to take place in acetic acid solution, a mixture of the diazine with a dihydrodiazine; whilst, in the case of dibenzoylstilbene, a dihydrodiazine is the sole product. *α*-Benzoyl-*β*-trimethacetylstyrene, however, yields a diazine only.

Experimental.

Preparation of Dibenzoylstyrene, $\begin{matrix} C_6H_5\cdot C = CH \\ C_6H_5\cdot CO \quad CO\cdot C_6H_5 \end{matrix}$.—The *cis*-form of this compound, melting at 129°, is readily obtained by the method described by Japp and Klingemann (*loc. cit.*, p. 672) of warming a mixture of benzil and acetophenone with alcoholic potassium hydroxide containing a little water. Johannes Wislicenus and Lehmann (*Annalen*, 1898, **302**, 196), who had overlooked Japp and Klingemann's work, recommend the use of alcoholic sodium hydroxide (without the addition of water) as a condensing agent. This is quite the reverse of an improvement; for, according to the statements of these investigators, a further condensation of the dibenzoylstyrene with acetophenone to dibenzoyldiphenylbutadiene occurs under these conditions, and from the latter substance the dibenzoylstyrene has to be freed by recrystallisation.

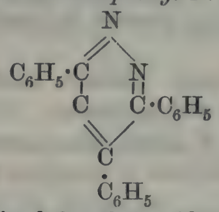
We find that *iso*dibenzoylstyrene (m. p. 197—198°), the *trans*-form—which was obtained by Japp and Klingemann only in quantity sufficient for analysis, and that, too, under conditions that could not always be depended upon to yield the compound—is present in small but fairly constant amount in the dark-coloured, aqueous-alcoholic, alkaline filtrate from the *cis*-dibenzoylstyrene obtained in the initial process of condensation. If this filtrate is diluted with water, the tarry precipitate steam-distilled to remove unaltered acetophenone, the non-volatile residue dissolved in alcohol, the solution boiled with animal charcoal, concentrated, and allowed to stand, a small quantity of *trans*-dibenzoylstyrene is deposited in slender colourless needles (m. p. 197—198°). The yield is, however, so unsatisfactory that we were obliged to prepare large quantities of the *cis*-compound in order to obtain about 2 grams of its *trans*-isomeride.

Action of Hydrazine on Dibenzoylstyrene.—Dibenzoylstyrene (m. p. 129°) was mixed with 1 mol. proportion of a 50 per cent. solution of hydrazine hydrate and heated in glacial acetic acid solution in an open flask on the water-bath for 15 minutes.

The experiment was repeated, using 2 mol. proportions of hydrazine hydrate.

In both cases the product, precipitated by water and crystallised either from alcohol or from benzene, consisted of a mixture of flat prisms or plates, which formed the chief product, with a small quantity of slender needles, the larger proportion of hydrazine hydrate giving a slightly improved yield of the latter compound. The two substances were separated by levigation with the mother liquor, the lighter needles being readily floated off.

The flat prisms or plates were purified by recrystallisation from benzene or alcohol. From the former solvent the substance was deposited in tables, from the latter in scales, melting at 170°. It was identical with Alexander Smith's 3 : 4 : 6-*triphenyl*-1 : 2-*diazine*,



(m. p. 171°, Smith), obtained by the oxidation of 3 : 4 : 6-triphenyl-1 : 2-dihydro-1 : 2-diazine (*Annalen*, 1896, **289**, 319), as we found by comparing our specimen with one prepared by Smith's method.

0·3427 gave 28·8 c.c. moist nitrogen at 10° and 759 mm. N = 9·00.
$C_{22}H_{16}N_2$ requires N = 9·09 per cent.

The needles were purified by recrystallisation, first from boiling alcohol and afterwards from glacial acetic acid. They were redeposited in slender, colourless needles, with a satiny lustre and melting at 181·5—182·5°, with decomposition, when rapidly heated. The crystals turned yellow on exposure to light.

0·1609 gave 0·5017 CO_2 and 0·0894 H_2O. C = 85·03 ; H = 6·17.
0·1903 „ 14·50 c.c. moist nitrogen at 13° and 758 mm. N = 8·98.
$C_{22}H_{18}N_2$ requires C = 85·16 ; H = 5·81 ; N = 9·03 per cent.

This is the formula of a 3 : 4 : 6-*triphenyldihydro*-1 : 2-*diazine*. The position of the two additive hydrogen atoms remains for the present undetermined. The substance is not identical with Alexander Smith's 3 : 4 : 6-triphenyl-1 : 2-dihydro-1 : 2-diazine (m. p. 186—188°, when quickly heated) (*Annalen*, 1896, **289**, 316), obtained by the interaction of desylacetophenone with hydrazine, a specimen of which we prepared for comparison. Smith's compound is of a bright yellow colour, and was oxidised to 3 : 4 : 6-triphenyl-1 : 2-diazine in an attempt which we made to acetylate it by means of acetic anhydride containing a little concentrated sulphuric acid ; in fact Smith had already oxidised it to this compound by treatment with chromium trioxide. Our isomeride, on the other hand, is colourless ; an attempt to acetylate it yielded only a resinous mass ; and we were quite unable to obtain the diazine from it by oxidation.

We afterwards found that by warming dibenzoylstyrene (m. p. 129°) with an excess of hydrazine in alcoholic (instead of acetic acid) solution on the water-bath for 15 minutes, an excellent yield of 3 : 4 : 6-triphenyl-1 : 2-diazine, without any admixture of the dihydro-compound, was obtained.

We also found that none of the dihydro-compound is formed when the diazine is boiled with hydrazine hydrate in acetic acid solution. In fact sodium in boiling alcohol has no action on the diazine. The reduction by hydrazine, to which the formation of the dihydro-compound is due, must, therefore, precede the condensation in which the diazine is formed.

The experiment was tried whether *iso*dibenzoylstyrene (m. p. 197—198°) would interact with hydrazine. After boiling the mixture in alcoholic solution for 6 hours, the *iso*-compound was recovered unchanged. *iso*Dibenzoylstyrene is therefore the *trans*-modification.

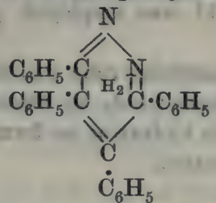
Action of Hydrazine on Dibenzoylstilbene, $\begin{matrix} C_6H_5\cdot C{=\!=}C\cdot C_6H_5 \\ C_6H_5\cdot CO \quad CO\cdot C_6H_5 \end{matrix}$.—Dibenzoylstilbene (m. p. 220°), regarded by Japp and Klingemann (*loc. cit.*) as the *cis*-form, was obtained by Zinin by the oxidation of tetraphenylfurfuran ("lepiden") with nitric acid, and was termed by him "acicular oxylepiden." By heating it with alcoholic potassium hydroxide he converted it into the isomeric "octahedral oxylepiden" (m. p. 232°), which Japp and Klingemann formulate as *trans*-dibenzoylstilbene. That both these compounds are dibenzoylstilbenes is proved by the fact that, on reduction, they both yield tetraphenylfurfuran. The dibenzoylstilbenes used in the following experiments were prepared by Zinin's methods (Beilstein's *Handbuch*, 3rd ed., **3**, 311 and 312).

Three grams of dibenzoylstilbene (m. p. 220°) and 1·2 grams of a 50 per cent. solution of hydrazine hydrate were dissolved in absolute alcohol and boiled for 1½ hours. On cooling, the solution deposited yellow needles which, by repeated recrystallisation from boiling alcohol, were obtained with the constant melting point of 207—208°. The yellow colour was not removed by boiling the solution with animal charcoal. The compound is difficult to burn and the figures for carbon are somewhat low.

0·1752 gave 0·5544 CO_2 and 0·0934 H_2O. C = 86·30 ; H = 5·94.
0·1774 „ 0·5594 CO_2 „ 0·0942 H_2O. C = 85·99 ; H = 5·90.
0·1763 „ 0·5570 CO_2 „ 0·0934 H_2O. C = 86·16 ; H = 5·89.
0·1722 „ 10·65 c.c. moist nitrogen at 11° and 757 mm. N = 7·34.
$C_{28}H_{22}N_2$ requires C = 87·05 ; H = 5·70 ; N = 7·25 per cent.

This is the formula of a tetraphenyldihydrodiazine. The formula of a tetraphenyldiazine, $C_{28}H_{20}N_2$, on the other hand, would require C = 87·50 ; H = 5·21 ; N = 7·29 per cent., and for this the value found for hydrogen is much too high. A portion of the hydrazine has therefore exercised a reducing action as in the case already described.

The compound is a 3 : 4 : 5 : 6-*tetraphenyldihydro*-1 : 2-*diazine*,



in which the position of the two additive hydrogen atoms has not yet been determined.

Dibenzoylstilbene (m. p. 232°)—"octahedral oxylepiden"—was then boiled with excess of hydrazine hydrate in alcoholic solution for 9 hours, renewing the hydrazine hydrate. On allowing the solution to cool, practically the whole of the dibenzoylstilbene (m. p. 232°) crystallised out unchanged. No new product could be detected.

The dibenzoylstilbene melting at 220° is therefore the *cis*-form; that melting at 232° the *trans*-form.

Action of Hydrazine on a-Benzoyl-β-trimethacetylstyrene,

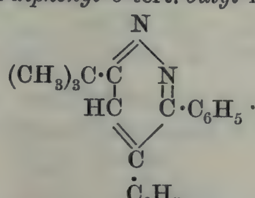
$$\begin{array}{l} C_6H_5\cdot C{=}CH \\ C_6H_5\cdot CO\ \ CO\cdot C(CH_3)_3 \end{array}$$

(m. p. 115°).—*a*-Benzoyl-*β*-trimethacetylstyrene was obtained by Japp and Maitland (Trans., 1904, **85**, 1496) by the condensation of benzil with methyl *tert*.-butyl ketone under the influence of alcoholic potassium hydroxide.

A mixture of benzoyltrimethacetylstyrene with an excess of hydrazine hydrate was dissolved in alcohol and boiled for 15 minutes. On cooling, the solution deposited wedge-shaped crystals, which, after recrystallisation from alcohol, melted constantly at 185—186°. The yield was good.

0·1738 gave 0·5288 CO_2 and 0·1094 H_2O. C = 82·98; H = 6·99.
0·1554 „ 12·97 c.c. moist nitrogen at 11° and 731 mm. N = 9·57.
$C_{20}H_{20}N_2$ requires C = 83·33; H = 6·95; N = 9·72 per cent.

The compound is 3 : 4-*diphenyl*-6-tert.-*butyl*-1 : 2-*diazine*,



Neither in the foregoing experiment, nor in one in which boiling acetic acid was used as a solvent for the interacting substances, could

any trace of the corresponding dihydrodiazine be detected. The experiment in which acetic acid was employed yielded a very resinous product.

The α-benzoyl-β-trimethacetylstyrene melting at 115° is the only known form of this substance; but, as already mentioned, the ease with which it interacts with hydrazine to form a diazine leads us to assign to it the *cis*-configuration.

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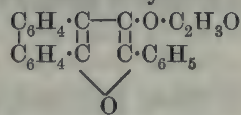
Condensations of Phenanthraquinone with Ketonic Compounds.

By Francis Robert Japp, F.R.S., and James Wood, M.A., B.Sc., Carnegie Scholar in the University of Aberdeen.

Very few condensations of phenanthraquinone with ketonic compounds have hitherto been studied, and in these only alkaline condensing agents have been employed; but in many cases such agents give no result.

We find, however, that acetic anhydride containing a little concentrated sulphuric acid frequently brings about the desired condensation. The reaction is occasionally complicated by the fact that in some cases the condensation product interacts further with the acetic anhydride.

3-*Acetoxy*-2-*phenyl*-4 : 5-*diphenylenefurfuran*, 

(m. p. 232°).—Twenty grams of finely-powdered phenanthraquinone (free from anthraquinone*), 14 grams of acetophenone, 130 c.c. of acetic anhydride, and 50 drops of concentrated sulphuric acid, were introduced into a flask fitted with a short open tube, and the flask was immersed in water kept at a temperature of 40—50°, whilst the mixture was shaken from time to time. In the course of 30—40 hours the whole of the phenanthraquinone had disappeared, and the liquid was filled with long, slender, almost colourless needles; these were separated by filtration and purified by recrystallisation from boiling benzene, decolorising with animal charcoal if necessary. The substance was thus obtained in slender needles, melting at 232°. The yield was 20 grams.

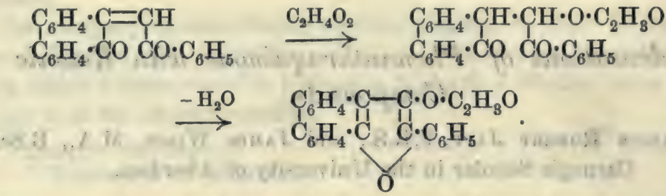
0·1386 gave 0·4139 CO_2 and 0·0576 H_2O. C = 81·44; H = 4·62.
0·1757 „ 0·5246 CO_2 „ 0·0744 H_2O. C = 81·43; H = 4·71.
$C_{24}H_{16}O_3$ requires C = 81·82; H = 4·55 per cent.

The formation of this compound may be explained on the assumption that the unknown phenanthroxyleneacetophenone,

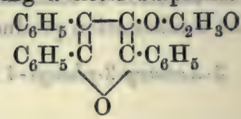
$$\begin{array}{l} C_6H_4\cdot C{=}CH \\ C_6H_4\cdot CO\ \ CO\cdot C_6H_5 \end{array},$$

* The phenanthraquinone used for these reactions must be purified by means of the hydrogen sodium sulphite compound, as some of the products are almost impossible to separate from the anthraquinone which will otherwise contaminate them.

is first formed; this compound then unites with acetic acid, and the additive compound parts with water:



The compound would thus be 3-*acetoxy*-2-*phenyl*-4 : 5-*diphenylenefurfuran*, and the transformation of the hypothetical intermediate product, phenanthroxyleneacetophenone, is strictly analogous to that which dibenzoylstyrene, $\begin{array}{l} C_6H_5\cdot C{=}CH \\ C_6H_5\cdot CO\ \ CO\cdot C_6H_5 \end{array}$, undergoes when it is converted, by the action of acetic anhydride containing a little sulphuric acid, into 3-acetoxy-2 : 4 : 5-triphenylfurfuran,



(J. Thiele, *Ber.*, 1898, **31**, 1248).

Ethyl Diphenylenedibenzoylmuconate (*Ethyl* $\beta\gamma$-*diphenylene*-$a\delta$-*dibenzoylbutadiene*-$a\delta$-*dicarboxylate*), $\begin{array}{l} C_6H_4\cdot C{:}C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5 \\ C_6H_4\cdot C{:}C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5 \end{array}$.—Ten grams of finely powdered phenanthraquinone, 12 grams of ethyl benzoylacetate, and 40 c.c. of acetic anhydride containing 16 drops of concentrated sulphuric acid were employed in this experiment, which was conducted like that already described. After heating continuously at 40—50° for nearly 100 hours, the whole of the phenanthraquinone had disappeared. The mixture was allowed to cool; the crystalline product was separated by filtration, washed with a little cold glacial acetic acid, and recrystallised from boiling benzene, in which it is fairly soluble. It was thus obtained in clear, rectangular plates with bevelled edges (yield: 10 grams). It softens and almost melts between 170° and 174°, but immediately resolidifies, finally melting sharply at 223°. This latter melting point, however, is that of an isomeride into which the original condensation compound is transformed by heating (*vide infra*).

0·1912 gave 0·5433 CO_2 and 0·0883 H_2O. C = 77·49; H = 5·13.
0·1705 „ 0·4838 CO_2 „ 0·0784 H_2O. C = 77·39; H = 5·11.
0·1832 „ 0·5200 CO_2 „ 0·0846 H_2O. C = 77·39; H = 5·13.
$C_{36}H_{28}O_6$ requires C = 77·70; H = 5·04 per cent.

The compound, which is *ethyl diphenylenedibenzoylmuconate* (*vide*

supra), is formed from phenanthraquinone and ethyl benzoylacetate according to the equation:

$$\begin{array}{l}C_6H_4\cdot CO\\ |\qquad\quad |\\ C_6H_4\cdot CO\end{array} + 2C_6H_5\cdot CO\cdot CH_2\cdot CO_2\cdot C_2H_5 =$$

$$\begin{array}{l}C_6H_4\cdot C{:}C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5\\ |\qquad\quad |\\ C_6H_4\cdot C{:}C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5\end{array} + 2H_2O,$$

the acetic anhydride in this case furnishing no part of the resultant molecule.

Attempts to hydrolyse this ester with alcoholic sodium hydroxide yielded no definite product. No acid could be obtained from the alkaline solution.

Isomeride (m. p. 223·5°) *of Ethyl Diphenylenedibenzoylmuconate.*—Five grams of ethyl diphenylenedibenzoylmuconate were heated in a test-tube by means of a glycerol bath until the substance, after softening and resolidifying between 170° and 174°, as above described, finally melted at 223°. No gas was given off during the process, and the tube with the product was found to weigh practically the same as before. The product was recrystallised from boiling glacial acetic acid, from which it was deposited in short yellowish needles, melting constantly at 223·5°. The yield is quantitative.

0·1635 gave 0·4646 CO_2 and 0·0756 H_2O. C = 77·49 ; H = 5·14.
$C_{36}H_{28}O_6$ requires C = 77·70 ; H = 5·04 per cent.

The compound is therefore isomeric with ethyl diphenylenedibenzoylmuconate. Provisionally it may be named *ethyl* iso*diphenylenedibenzoylmuconate.*

Hydrolysed with alcoholic sodium hydroxide it yields an acid, which, however, has not yet been obtained in quantity sufficient for examination.

The fact that ethyl diphenylenedibenzoylmuconate, unlike its isomeride, does not yield an acid under the foregoing conditions, points to a difference in constitution between the two compounds more fundamental than that of mere *cis* and *trans* isomerism—the explanation which would perhaps first suggest itself. Possibly the isomerisation under the influence of heat occurs according to the scheme:

$$\begin{array}{l}C_6H_4\cdot C{:}C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5\\ |\qquad\quad |\\ C_6H_4\cdot C{:}C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5\end{array} \longrightarrow \begin{array}{l}C_6H_4\cdot C\cdot C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5\\ |\qquad\quad |\ \ |\ \ |\\ C_6H_4\cdot C\cdot C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5\end{array},$$

in which case ethyl diphenylenedibenzoylmuconate would have somewhat the same relation to ethyl *iso*diphenylenedibenzoylmuconate that cinnamic acid has to β-truxillic acid, except that in the present case the polymerisation is intramolecular, not intermolecular.

We have also obtained condensation products of phenanthraquinone with ethyl acetoacetate and with ethyl malonate. We wish to reserve the study of the various condensations of this class.

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